

MULTIPLE-PROCESS SORPTION OF NITROGEN HETEROCYCLIC
COMPOUNDS ON SOILS AND SURFACTANT-MODIFIED CLAYS



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By

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Sorption of three ionizable nitrogen heterocycles (NHCs)—2-methylpyridine, quinoline, and acridine—was investigated to determine the relative contributions of the neutral and protonated species to overall sorption. Batch sorption experiments were conducted on both soils and surfactant-modified clays (organoclays), which were synthesized from the exchange of hexadecyltrimethylammonium (HDTMA) cations for resident sodium cations on a specimen smectite (Swy-2) at 0, 60, 80, and 100% of the cation exchange capacity. HDTMA exchange creates highly effective organic partitioning domains within clay interlayers. The fractionally exchanged clays, therefore, provided discrete exchange and organic partitioning domains for both the protonated and neutral species of the NHCs. Data were described by a combined Langmuir-linear isotherm that permitted independent characterization of both sorption components. Although adsorption of the cation can dominate the overall process, both species contributed substantially to sorption depending on pH.

Based on these findings, the combined isotherm was applied to sorption by soils possessing a range of properties relative to pH, organic carbon content, and cation exchange capacity. Results indicated that cationic sorption dominated, but that the neutral species can contribute substantially given sufficient sorbent organic carbon content relative to the CEC. The data also indicated that the contribution of the neutral species to overall sorption was relatively consistent for all three compounds.

CHAPTER 1 INTRODUCTION: PROCESSES GOVERNING THE SORPTION OF ORGANIC BASES

Introduction

Organic bases are an important class of contaminants whose fate in the environment deserves attention. They are most prevalent as pesticides (e.g., the triazine herbicides) and as basic nitrogen heterocyclic compounds (NHCs) such as pyridine, quinoline, and acridine. In addition to direct toxicity, the environmental importance of these chemicals is compounded by their frequently low molecular weights and high water solubilities, which can enhance their mobility and their ability to impact human health.

Triazine herbicides such as atrazine, simazine, and cyanazine, primarily are applied to crops like corn and sorghum, although they have also been used for weed control in fruit orchards and on vegetable crops (Gast, 1970). Solubilities, organic carbon partitioning coefficients, and acid dissociation constants vary widely among this class of compounds; thus, concentrations in the environment are controlled through interactions with both soil organic matter and clay mineral surfaces (Hayes, 1970). Amphoteric herbicides (e.g., imazaquin), which contain both acidic and basic functional groups, are similarly influenced by both organic and mineral sorbent components subject to pH.

NHCs are most commonly found in energy-associated wastes such as shale oil retort wastewaters, coal tar derivatives, and coal tar processing wastes derived from the conversion of fossil fuels to synthetic fuels (Periera et al., 1983; Leenheer et al., 1982). N-heterocycles also have been associated with surface and subsurface waters near coal

liquification facilities (Sims and O'Loughlin, 1989). Coal tar is produced from the distillation of bituminous coal and is diverse in its composition. Periera et al. (1983) isolated 47 N-heterocyclic compounds including 5 quinoline, 3 acridine, and 6 pyridine derivatives from ground waters near a coal tar distillation facility in Minnesota. A similar array of compounds was identified in oil shale retort waters (Leenheer et al., 1982) where, for example, combined concentrations of substituted pyridines exceeded 1300 mg/L. Therefore, environmental loadings of these compounds can be substantial, necessitating a greater understanding of the mechanisms governing their proliferation in the environment.

Critical to the environmental fate of NHCs is their ability to speciate in solution subject to pH. By definition, NHCs contain nitrogen moieties capable of accepting protons and becoming positively charged (eq. 1.1)



where R-N is the neutral nitrogenous base and R-NH⁺ is the protonated form. Overall sorption of NHCs in soils and aquifers can potentially stem from a number of mechanisms, including exchange of the cation, solvophobic partitioning of the neutral species, cooperative sorption resulting from interactions with previously sorbed species, and chemisorption at colloid surfaces. A comprehensive treatment of total sorption, therefore, would require discrimination among all of the potential individual contributions. This would be unwieldy for most applications. However, the two mechanisms that apparently dominate sorption are those which control the analogues of the two organic base species: exchange of the cation, and partitioning of the neutral

species into organic carbon (Nichols and Evans, 1991; Ainsworth et al., 1987; Zachara et al., 1986; Hasset et al., 1983; Banwart et al., 1982).

Exchange of organic base cations has been demonstrated or inferred by a number of investigators. Observations include a decline in sorption with increased pH and ionic strength; correlation of sorption with the ionized species fraction in solution and with the CEC; a vulnerability to competition from other cations; and a body of spectroscopic evidence (Traina and Onken, 1991; Ainsworth et al., 1987; Zachara et al., 1986; Zierath et al., 1980). The neutral species can be retained in soils and sediments through hydrophobic interactions that have been correlated with soil organic carbon content (Banwart et al., 1982). The relative abundance of organic carbon compared to silicate clays also can serve as a mitigating factor for substantial sorption of the neutral species (Zachara et al., 1986; Hasset et al., 1983).

Thus, depending upon the system pH and base character of the sorbate, the potential exists for describing organic base sorption using model analogues for permanent cations and for neutral organic molecules. The present goal is to determine if evaluation of these two primary components can be employed independently to approximate the potentially more complicated overall process. Soil reactions of organic bases, therefore, will be assumed to result from essentially two factors: speciation of the base as described above, and the relative abundance of organic and inorganic components in the sorbent phase with which a given species may interact.

Sorption of Inorganic Cations

For 2:1 layer silicates, charge arises from isomorphic substitution in the tetrahedral and octahedral sheets of clay minerals, or from pH-dependent deprotonation

of hydroxyl groups located at mineral edges. Charge on organic matter is also pH-dependent and due to deprotonation of carboxylic, phenolic, or other acidic functional groups in the organic matrix.

Selectivity of cations for these negatively charged sites is dictated by essentially two factors: the valence of the cation and its size. Highly charged cations are more strongly attracted to negatively charged sites, however their ability to closely approach these sites is constrained ultimately by their overall hydrated size or volume. Cations with a small crystallographic (dehydrated) radius are able to attract water of hydration more strongly, resulting in generally larger hydration spheres, which moderate electrostatic interactions with negatively charged sites. Thus, cations like Na^+ with a single charge and large hydrated radius are more weakly held at mineral surfaces, for example, than other group I cations like potassium or cesium, which have progressively smaller hydrated radii.

Adsorption of Organic Cations

Sorption of organic base cations appears is most commonly associated with the abundance of silicate clays, and also has been described as a function of the sorbent cation exchange capacity (Ainsworth et al., 1987; Zachara et al., 1986). Exchange of *permanent* organic cations is well established, as is their relatively high stability at mineral surfaces. However, in contrast to metallic cations, exchange selectivity and organic cation stability is due to the concerted impacts of Coulombic (electrostatic) and non-Coulombic (van der Waals) interactions of the charged and carbonaceous moieties of organic cations with colloid surfaces. Fig. 1.1 shows schematically the interaction of a 16-carbon aliphatic organic cation with an idealized mineral surface. The electron-

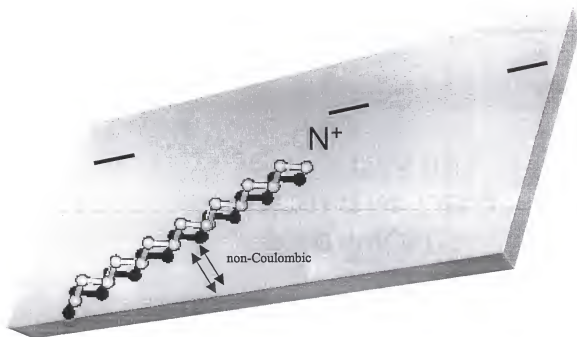


Figure 1.1. Schematic of an adsorbed alkylammonium cation on a colloid surface (Coulombic and non-Coulombic Interactions).

deficient component of the ion (centered on the nitrogen atom) is electrostatically attracted to negatively-charged sites at the clay surface, with adsorption being augmented by primarily van der Waals interaction of the hydrocarbonaceous alkyl "tail" with the siloxane surface. This exposed surface can be regarded as essentially neutral, based upon research with unsubstituted 2:1 layer silicates such as pyrophyllite and talc, and also with other clays that have been exchanged with short-chain aliphatic organic cations. These weakly-hydrated ions occlude negatively charged sites, but expose the surfaces *between* sites, permitting their direct interaction with other solution species. Such interactions have proven to be generally van der Waals in nature, yielding strong subsequent uptake of the neutral hydrophobic analogues (e.g. benzene) of many NHCs (Lee et al., 1989).

The impact of van der Waals forces in the exchange of organic cations was recognized as early as 1939 (Hendrix, 1940). Later, Cowan and White (1958) showed that exchange selectivity for n-primary aliphatic amines on montmorillonite increased with carbon substitution into the cation, implying profound contributions to surface stability from these substituents. Subsequent examinations determined that the Gibbs free energy of exchange could be related to chain length of the n-alkylammonium cations. Fig.1.2 suggests that the exchange energy is composed of two free energy components: electrostatic interaction with the surface charges as indicated by one component of the overall Gibbs free energy (ΔG_{elect}), plus hydrophobic interaction (ΔG_{hyd}) of the alkyl carbons with the remaining (neutral) clay surface. The intersection along the ordinate in Fig 1.2 reflects the magnitude of the electrostatic contribution to the free energy, which sets a lower limit based on simple, "non-augmented" exchange similar to that for

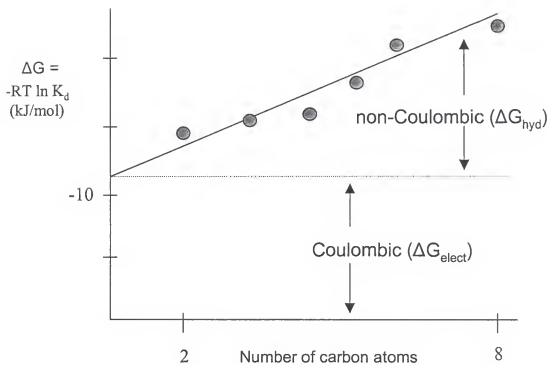


Figure 1.2. Relationship between the energy of adsorption and the number of carbon atoms in the alkyl substituent. K_d is a sorption coefficient, ΔG is the Gibbs free energy, R is the ideal gas constant, and T is the temperature. Adapted from Cowan and White (1958)

inorganic metal cations. With each carbon addition to the alkyl chain, however, the energy of adsorption increased systematically. Mechanistically similar contributions to stabilization of organic cations on clay surfaces have been observed for a variety of both aliphatic and aromatic compounds (Jaynes and Boyd, 1991; Margulies et al., 1988, Narrine and Guy, 1981).

Among the more exhaustively investigated organic cations are the monovalent organic dyes, including methylene blue, thionine, and malachite green. Many are compositionally similar to NHCs and are characterized by heterocyclic ring systems, with the charge originating from bound nitrogen. Thus, dye cations can possess a large hydrophobic surface area in relation to their charge, which promotes stability at mineral surfaces as described above. Binding coefficients for methylene blue, for example, may be several orders of magnitude greater than for sodium (Margulies et al., 1988).

In addition to these highly selective exchange reactions, sorption frequently is characterized by the formation of surface aggregates involving two or more dye molecules. This can lead to sorption in excess of the CEC (Rytwo et al., 2000; Narine and Guy, 1981). In essence, solution cations are subject to both electrostatic interactions with charged surface sites and non-specific hydrophobic interactions with previously sorbed species. Spectroscopic evidence suggests that dimeric and trimeric surface species of methylene blue can form at less than 2% of the CEC (Cenens and Shoondheydt, 1988), but initiation of dye aggregation ultimately depends on the adsorbent, cation composition, surface coverage, solution cation concentrations, and ionic strength (Neumann et al., 2000; Mishael et al. 1999; Narrine and Guy, 1981). Despite these mitigating factors it

appears that adsorbed dye molecules may function as nuclei for polymeric species that can promote sorption in excess of the CEC.

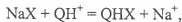
Sorption in excess of the mineral CEC also has been observed for a number of alkylammonium cations, including hexadecyltrimethylammonium (Bonczek et al., 2002; Jaynes and Boyd, 1991). In this case, however, aggregation of surface species for sorption below the CEC was not necessarily observed. Instead, measurements of montmorillonite basal spacings for incremental HDTMA exchange at sorption levels below the CEC indicated that either monolayers or bilayers, rather than surface aggregates, dominated the interlayer (Bonczek et al., 2002). Thus, stoichiometric sorption of HDTMA cations up to the CEC ultimately creates strongly hydrophobic organic phases in clay interlayers that can interact with the alkyl tails of incoming solution species (Jaynes and Boyd, 1991). Similar mechanisms account for surfactant bilayer formation on zeolite surfaces in excess of the CEC (Zhaohui and Bowman, 1997). Alkylammonium cations sorb primarily to the external surfaces of zeolites, forming monolayers at surface loadings up to the CEC. Beyond the CEC, however, interactions among the hydrocarbonaceous substituents of adsorbed and solution cations lead to eventual formation of a bilayer pseudo-phase.

Sorption of other permanent organic cations, including divalent paraquat and diquat herbicides, also is driven ultimately by cation exchange. However, the presence of an additional charge on the ion necessitates a greater emphasis on the adsorbate's orientation at charged surfaces, as well as a need to consider the charge properties of the mineral (Rytwo et al., 1996; Weed and Weber, 1969). Paraquat and diquat are structurally similar, but diquat generally is sorbed at levels above the CEC on

montmorillonite while paraquat exchange commonly *equals* the CEC. This difference is ordinarily attributed to the degree of charge separation within the ion, which equals approximately 0.71 nm for paraquat and 0.29 nm for diquat. Diquat apparently can “key” into the ditrigonal cavity of the clay surface, and also may be more susceptible to non-coulombic interactions with previously adsorbed species (Chen et al., 1999; Rytwo et al., 1996).

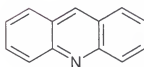
Organic Base Cations

With regard to organic *base* cations, sorption is expected to be fundamentally similar to that for permanent organic cations. Many are aromatic heterocycles and, thus, are structurally related to cationic dyes like methylene blue (Fig. 1.3). However, they also can exist as single or multi-ring systems, precluding simple, definitive extrapolation of behavior based strictly on related compounds. Nonetheless, organic bases, particularly NHCs like those to be examined here, feature a single charge paired to a comparatively large hydrophobic substituent. Thus, they are bound at mineral surfaces by both Coulombic and non-Coulombic forces, which can promote highly selective exchange in a manner similar to that for permanent organic cations (Chorover et al., 1999; Zachara et al., 1990; Ainsworth et al., 1987). Further, sorption similarly is linked to the size of the aromatic substituent on the cation. For example, sorption of three simple NHCs has been shown to proceed in the order: acridine (3 rings) > quinoline (2 rings) > pyridine (1 ring). Additionally, based on the reaction:

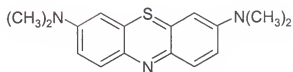




Quinoline



Acridine



Methylene Blue

Figure 1.3. Structures of 2 N-heterocycles in relation to methylene blue

Vanselow selectivity coefficients (K_v) calculated from quinolinium-sodium exchange on Na-montmorillonite have been shown to range between 200 and 1200 (Ainsworth et al., 1987) based on eq. 1.2.

$$K_v = X_{QH} * (Na^+) / X_{Na} * (QH^+) \quad (1.2)$$

where X_{QH} and X_{Na} are mole fractions of quinolinium and sodium on the exchanger, and parentheses indicate solution cation activities. These types of selectivity coefficients ordinarily are not determined for organic dyes like methylene blue, since monomers, dimers, and trimers may be adsorbed. However, estimated binding coefficients for methylene blue monomers are typically several orders of magnitude greater than those for Na^+ or Ca^{2+} , indicating particularly selective exchange. Quinoline is a two-ring system, whereas methylene blue is a three-ring system and also possesses additional carbonaceous groups (Fig. 1.3). Therefore, quinoline has a somewhat smaller hydrophobic surface area, constraining its interaction with siloxane surfaces. This property also may moderate quinoline's inclination to form aggregates at mineral surfaces, or to resist competition from other cations (Chorover et al., 1999). Interactions of pi electron systems between aggregating molecules—which, in part, determines the process—is a function of ion size in relation to charge. Thus, a reduction in the size of the hydrophobic portion of the cation also favors a reduced tendency to aggregate. For example, “new” methylene blue, which contains two additional ethyl groups, aggregates to a greater extent on montmorillonite than methylene blue (Narrine and Guy, 1981).

N-heterocycles like pyridine and quinoline are smaller still, perhaps further moderating the impact of aggregation. No molecular pyridine sorption was observed at $pH > 7$ on kaolinite and montmorillonite (Baker and Luh, 1971). However,

Ainsworth et al. (1987) argued for a type of pH-dependent, surface-mediated association between quinoline molecules, perhaps through the formation of surface "hemisalts" as shown in Fig. 1.4 and via Eq. 1.2 (Ainsworth et al., 1987; Mortland, 1970):



Their conclusions in this regard were highly interpretive, based on traditional equilibrium sorption isotherms at three pH levels in excess of the compound's pKa value. Data simulation using a power function apparently deteriorated somewhat with pH and surface coverage, leading to separate regression of data for subjectively chosen high and low solution concentrations. The result was determined to suggest the formation of specialized surface species involving sorption of the neutral molecule, the predominance of which increased with pH. Support was provided by the observation that concurrent hydrogen ion consumption (due to protonation of quinoline) during sorption declined at higher surface densities of quinoline which was again dependent upon pH. The shift to sorption of molecular species was determined to occur at approximately 50% coverage of the CEC at pH 5.5, and about 14% of the CEC at pH 7.5.

Spectroscopic evidence is at variance with these conclusions. Traina and Onken (1991) observed that no molecular quinoline was present at the surface of montmorillonite or hectorite at pH levels in excess of pH 7. They also failed to observe a systematic consumption of protons coincident with quinoline sorption up to 34% of the CEC at pH > 7. However, in a related study for acridine, there was evidence of clustered surface species involving neutral molecules (Chattopadhyay and Traina, 1999). Thus, there is an apparent contradiction that may be related to the relative size of the molecules,

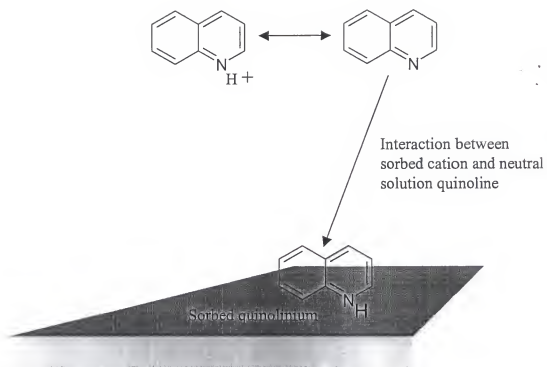


Figure. 1.4. Formation of a hemisalt at the clay surface.

concentrations of the adsorbate in solution, characteristics of the adsorbent, or solution ionic strength. Nonetheless, the "hemisalts" postulated by Ainsworth et al. (1987) are fundamentally similar to aggregates because they involve interactions between sorbed and solution species. Therefore, they may account for some macroscopic observations suggesting greater-than-anticipated sorption of quinolinium based strictly on pH and quinoline's acid dissociation constant (Nichols and Evans, 1991; Zachara et al., 1986; Helmy et al., 1983).

For example, evidence of increased sorption at pH levels above the compound's pKa value has been reported (Helmy et al., 1983). for high solution quinoline concentrations on pure clays. This behavior was explained in terms of decreased competition from H^+ as the pH increased, and by associations among neutral species at the clay surface as described above. The authors believed that the neutral molecule was especially well accommodated at montmorillonite surfaces by this process, leading to greater sorption as the pH approached 6. They estimated that two-thirds of the adsorbed molecules were neutral at this pH. It should be noted, however, that solution quinoline concentrations were as high as 17 $\mu\text{mol/ml}$, which would tend to strongly facilitate such reactions (Traina and Onken, 1991; Maugulies et al., 1988; Ainsworth et al., 1987).

Alternatively, Nichols and Evans (1991) postulated that surface protonation reactions (Voudrias and Reinhard, 1986; Karickhoff and Bailey, 1976; Mortland, 1970) for organic bases permitted cation adsorption at bulk solution pH levels above the solute's pKa value. Surface protonation of ionizable organic and inorganic species due to clay surface acidity has been noted by several investigators. In essence, water molecules coordinated to exchangeable cations at silicate surfaces may donate protons to basic

molecules in solution near charged sites (Bronsted acidity). However, the overall extent depends intimately upon temperature, the nature of the adsorbate, its pKa, the exchangeable inorganic cation, degree of hydration, and the nature of the adsorbent (Voudrias and Reinhard, 1986; Bailey et al., 1969). The conclusions of Nichols and Evans (1991) were based on the observation that the pH where the sorption coefficient k_d ($k_d = S_e/C_e$; where S_e is the amount sorbed and C_e is the equilibrium solution concentration) was one half its maximum value was more than 1 pH unit greater than (not equal to) the pKa value of 4-methoxyaniline. At pH=pKa, the compound is 50% ionized. Based on cation exchange alone, Nichols and Evans (1991) assumed that sorption should be one-half the maximum value at this pH. This approach, however, assumes that the shape of the single-point isotherm was independent of the equilibrium concentration. In other words, it assumes that all the isotherms at different pH values are linear. It is clear, however, that sorption isotherms for organic bases are decidedly non-linear (Traina and Onken, 1991; Ainsworth et al., 1987; Zachara et al., 1986; Zierath et al., 1980). Additionally, surface protonation reactions can be both unpredictable and extremely slow (Voudrias and Reinhard, 1986).

Reports of chemisorption for organic base cations are essentially absent, except for reports of the potential for coordination reactions involving lone-pair electrons on anilines with transition metals on the exchange complex (e.g. Cu^{2+} and Fe^{3+} ; Voudrias and Reinhard, 1986; Cloos et al., 1979). Ordinarily, this type of electron-transfer reaction occurs only under desiccated conditions. However, such reactions have been shown to occur for aniline in aqueous systems. The reactions may have potential environmental importance, given the ubiquity of iron in natural systems.

Nonetheless, nitrogen heterocycles will be the principal focus of this work and, based on the above discussion, essentially two mechanisms apart from “ordinary” cation exchange have been implicated in their sorption on clay minerals: the formation of clusters or aggregates at mineral surfaces, and surface protonation reactions which essentially augment exchange itself. In either case, cation exchange is the ultimate driving force behind adsorption. Further, the magnitude of these “extraneous” forces has yet to be systematically established, and is subject to a number of mitigating factors as discussed above. Therefore, despite indications of molecular species contributions to sorption on clay minerals at pH levels more than a unit greater than the compound’s pK_a value, sorption of the cation largely can be viewed as an exchange phenomenon. Evidence is provided by increased sorption with decreased pH, competitive effects from inorganic cations, and the relationship between sorption and the CEC.

This simplification is desirable in the present context due to the difficulty in delineating multiple sorption mechanisms from traditional batch data. Moreover, while detailed mechanistic investigations are important for elucidating the overall impact on total sorption of cation interactions at mineral surfaces, the presence of organic matter, as well as that of the neutral species, additionally could alter equilibrium.

Interactions between organic cations and the soil organic fraction (including cation selectivity) are not particularly well documented. However, combined Coulombic and non-Coulombic interactions are expected. Electrostatic interactions are similar to those for organic cations on silicate clays, and the organic moieties of the cation are likely compatible with the carbonaceous matrix of organic matter.

Organic matter is conformationally flexible, which allows it to present its polar domains to the surrounding aqueous environment, and to shield its more carbonaceous domains. This is similar to the behavior of surfactant micelles in aqueous solution. Presumably, organic cations could align themselves so that their hydrocarbonaceous moieties are associated with the interior hydrocarbon domains on organic matter, while the charged, polar regions of the cation commingle with the oppositely charged domains.

The Neutral Form of Organic bases

Presumably, the neutral forms of organic bases are subject to similar solvophobic forces in the aqueous phase as are their aromatic counterparts. It is reasonable to expect, therefore, that in systems with sufficient organic carbon, their sorption also would be analogous. For example, chloro-s-triazine sorption has been related to organic carbon content for a number of soils and sediments (Baker et al., 1997; Karickhoff, 1981). Aniline sorption also has been described in relation to sorbent organic carbon content.

Data for the sorption of the neutral form of N-heterocycles is lacking, however. Some authors have conjectured that, in some instances, low solubility and relatively high polarity may moderate interactions of such molecules with soil or sediment organic domains (Zachara et al., 1986). Many neutral NHCs *are* polar; but sorption relative (normalized) to organic carbon is reported routinely for the polar forms of organic acids (Regitano et al., 2000; Che et al., 1992; Jafvert et al., 1990). Many NHCs also are quite soluble, which might moderate hydrophobic forces in the aqueous phase and limit interaction with soil organic carbon. However, benzene conforms to K_{oc} -solubility relationships with equal or greater statistical certainty than homologous compounds of lower solubility, like naphthalene and anthracene (Karickhoff, 1981). Benzene is the

polycyclic hydrocarbon analogue of the lowest molecular weight, highest solubility NHC (pyridine).

Nonetheless, only a few investigations have focused on the interaction of neutral NHC molecules with the organic fraction of soils or sediments. Banwart et al. (1982) examined sorption of three high molecular weight N-heterocycles—biquinoline, acridine and dibenzocarbazole—on sediments. They determined that sorption was driven by solvophobic partitioning into the sediment's organic component. Organic carbon contents ranged from 0.11 to 2.38% and sediment pH was between 4.5 and 8.5. Isotherms for these compounds were linear, and generally conformed to traditional K_{oc} - K_{ow} and K_{oc} -solubility relationships derived for a number of polynuclear aromatic hydrocarbons (Karickhoff et al., 1979).

Alternatively, Zachara et al. (1986) related sorption by soils to the ionized species in solution and the cation exchange capacity. In effect, an exchange-normalized Freundlich sorption coefficient, K_f/CEC , was strongly correlated with predominance of the exchangeable species in solution. However, their experiments were designed specifically to examine the role of organic *cations* in sorption; thus, they were conducted on soils of low organic carbon content, which would tend to obviate the impact of the neutral species on sorption and, therefore, K_f values. Of the nine soils used, six had organic carbon contents less than or equal to 0.35%, and all but one had organic carbon contents below 0.60%.

By comparison, eight of the sediments examined by Banwart et al. (1982) had organic carbon contents greater than the highest level tested by Zachara et al. (1986). This, combined with the much greater hydrophobicities of acridine, biquinoline, and

dicarbendazole relative to quinoline, likely contributed to the disparate results. For example, the octanol-water partitioning coefficient for quinoline is approximately 42 times less than that of acridine, and 200 times less than that of biquinoline. This led Zachara et al. (1986) to conclude that lower molecular weight, higher solubility compounds like quinoline would not be greatly subject to solvophobic forces in the aqueous phase. Thus, sorption would be almost entirely due to cation exchange.

The Relative Contributions to Sorption from the Neutral and Protonated Species

Based on the above discussion, the ability to observe uptake of the neutral species from solution in contact with both mineral and organic domains appears related to the strength of partitioning of the neutral molecule relative to adsorption of organic cations on clay minerals. Selectivity for organic cations is demonstrably high as discussed previously. Binding coefficients for organic cations range from between 10^5 for cations like crystal violet, and 10^8 for methylene blue (Rytwo et al., 1995). However, uptake of polar and non-polar neutral molecules is, in general, comparatively weak. For example, carbendazum and 1,4-nitroaniline, although structurally somewhat dissimilar, have approximately the same log octanol-water partitioning coefficients, 1.4 and 1.5, respectively (Hansch and Leo, 1979). Sorption of the two compounds at pH 7 on the same sandy clay loam (O.C. = 1.02%, CEC = 172 mmol(-)/kg) were approximately equal, and yielded sorption coefficients (k_d) of <2 ml/g (Nichols and Evans, 1991). Sorption of 1,4-nitroaniline was essentially constant with pH, but the k_d value for maximum sorption of carbendazum cations at pH 4 on the same soil exceeded 20 ml/g, suggesting that the cation was roughly 10 to 20 times more strongly sorbed than the neutral form of either compound. Similar relative magnitudes of neutral and protonated

species sorption were reported for four other organic bases on both the sandy clay loam indicated above and a sandy loam soil (Nichols and Evans, 1991).

Consequently, direct indications of the contribution of the neutral species to overall sorption of organic bases (relative to the cation) are essentially absent because the impact of cation adsorption naturally tends to obscure contributions from the neutral molecule when the two species coexist in the same system. This has led some investigators to the aforementioned inference that neutral organic bases may not be greatly subject to interactions with soil organic carbon, particularly bases of comparatively low molecular weight (Zachara et al., 1986). The argument can be made, however, that cation exchange and organic partitioning are related for organic bases because the same factors promote both mechanisms. Recall, that beyond the strictly electrostatic component to exchange of organic cations, is a *non-Coulombic* component. In essence, hydrophobic substituents on organic cations interact with mineral surfaces, appreciably augmenting exchange. This interaction is regarded as largely responsible for the tenacity with which organic cations are adsorbed. Thus, the molecular substituents responsible for highly selective exchange on soil clays also may play a role in the partitioning of organic compounds into the organic fraction of soils and sediments.

Clearly, organic partitioning is linked to the size of the neutral substituent of a molecule. Likewise, adsorption via exchange also depends on the size of the neutral portion (Fig 1.2). Therefore, as the size of the neutral portion of the sorbate and, consequently, its interaction with organic carbon declines, so does the strength of cation exchange and the ion's selectivity over other cations. Consider the N-heterocycles

acridine (3 rings), quinoline (2 rings), and pyridine (1 ring). Their log octanol-water partitioning coefficients are 3.40, 2.04 and 1, respectively, and their conditional exchange coefficients (conditional with respect to solid phase activities) vary similarly. The log of the conditional exchange coefficients, $\text{Log } K_{\text{ex}}$, for acridine, quinoline, and pyridine on Na-montmorillonite have been calculated as 3.00, 2.12, and 1.47, respectively (Zachara et al., 1990). Thus, the two sets of values do not diverge substantially, and the strength of organic partitioning relative to exchange may be less variable with molecular weight than might be expected. To put it more simply, as ring number on the base cations increases, both the exchange coefficient and the octanol-water partitioning coefficient increase by approximately equivalent proportions. So, the *relative* strengths of absorption and adsorption within the series of compounds may remain relatively constant. Thus, given sufficient organic carbon in relation to the CEC, sorption of the neutral species of lower molecular weight organic bases may be substantial.

To observe these contributions clearly requires conditions that favor sorption of the neutral species. The present work is designed to emphasize these conditions in an effort to elucidate the relative contributions of both NHC species to overall sorption. Quinoline first will be employed as a probe compound for sorption onto organoclays, whose ratios of organic carbon to CEC can be manipulated and controlled. Contributions to sorption from both base species will be deduced from the application of a combined Langmuir linear isotherm, which presumes both adsorption and organic partitioning of the compound based on pH and sorbent composition. These observations then will form the basis from which sorption will be estimated for soils.

CHAPTER 2 DESCRIBING SORPTION IN SOILS AND ORGANOCLAY SYSTEMS

Introduction

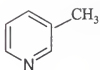
As discussed in Chapter 1, the nitrogen heterocycles (NHCs) to be studied here are capable of accepting protons and becoming positively charged. Thus, nitrogen heterocycles can exist as either the neutral or protonated species, depending upon pH. N-heterocycles were chosen because their sorption has been among the most thoroughly studied of organic bases. Additionally, hydrophobicity and exchange selectivity for NHCs have been shown to be systematically related to ring number (Zachara et al., 1990; Banwart et al., 1982), and the pKa values for the acidic forms of these compounds are within a pH range ordinarily encountered under natural conditions. Essential properties of the three NHCs to be employed here—2-methylpyridine, quinoline, and acridine—are listed in Table 2.1. The compound 2-methylpyridine was chosen over the more commonly studied base, pyridine, because of its pKa value, and its lower volatility. Structures are shown in Fig. 2.1.

Table 2.1. Properties of N-heterocycles.

Compound	molecular weight (g/mol)	pK _a ^{*1}	Log K _{ow} ^{*2}
2-methylpyridine	93.12	6.00	1.2
Quinoline	129.15	4.92	2.04
Acridine	179.19	5.68	3.4

^{*1} Perrin et al., 1981

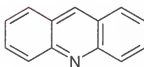
^{*2} Zachara et al., 1990.



2-methylpyridine



Quinoline



Acridine

Figure 2.1. Structures of three N-heterocycles.

Sorption of the protonated form of NHCs apparently is controlled by the paired influences of electrostatic and non-coulombic interactions at mineral surfaces in a manner that is analogous to the behavior of permanent charge organic cations. This combination of forces yields a high energy of adsorption and, thus, characteristically high selectivity for organic cations and protonated organic bases. For example, calculated Vanselow selectivity coefficients for quinoline can range between 200 and 1200 depending on pH (Ainsworth et al., 1987) and binding coefficients for monovalent organic dye cations can be several orders of magnitude greater than those for metallic cations like Na^+ or Ca^{2+} (Rytwo et al., 1995; Narrine and Guy, 1981). The high selectivity for organocations has led in turn to the inference that sorption of organic bases occurs largely by cation exchange. The contribution of the neutral species—depending on such factors as molecular weight, pH, polarity, and sorbent organic carbon content—frequently has been overlooked. However, limited research with NHCs at high pH in soils and sediments has implicated organic carbon and the neutral species of NHCs in sorption (Zachara et al., 1986; Hasset et al., 1983; Banwart et al., 1982). Thus, sorption in the present case will be described using model analogues for both organic base species.

Sorption Relationships

The Freundlich Isotherm

Equilibrium sorption of organic bases traditionally has been described almost exclusively by non-linear optimization of the Freundlich isotherm equation (Broholm et al., 1999; Ainsworth et al., 1987; Zachara et al., 1986; Baker and Luh, 1971):

$$S = K_f C^N \quad (2.1)$$

Here, K and N are coefficients derived from the linear log transform of the equation:

$$\text{Log } S = \text{Log } K_f + N \log C. \quad (2.2)$$

The Freundlich equation is the oldest non-linear sorption isotherm and has been widely used to describe the sorption of a broad range of solutes, in part because the presence of two model coefficients facilitates curve fitting to a variety of data. Its principal limitation, however, is that it does not encompass a sorption maximum. It also has no specific theoretical foundation, although it is sometimes regarded as indicative of multiple sorption mechanisms acting in concert (Brownawell et al., 1990).

Sorption of organic bases (and, in particular, NHCs) typically has been modeled using the Freundlich equation and is regarded largely as a cation exchange phenomenon. However, the Freundlich isotherm is not generally indicative of ion exchange, although efforts to relate sorption to the cation exchange capacity and compound ionization in low organic carbon substrates through the Freundlich relation have met with some success (Zachara et al., 1986). Thus, the Freundlich isotherm offers one avenue by which sorption might be predicted given knowledge of the appropriate coefficients, but it does not indicate the relative contributions of the neutral and protonated species to the overall process. This is particularly true for sorbents that possess significant organic carbon.

The Langmuir Isotherm

Adsorption/exchange of the cationic form of organic bases will be modeled using the Langmuir equation. This equation originally was developed to describe the sorption of gases by uniform pristine solid surfaces (Langmuir, 1918). The solid is assumed to have a finite set of discrete sorption sites, from which is derived one of the equation's most attractive features: an upper limit to adsorption. The equation is derived from a very simple reaction:



where A represents a gas molecule, and B represents the adsorbing surface. If M is the maximum adsorption capacity and n is the amount of gas adsorbed per unit area, then Z can be used to represent the fraction of the surface covered by the adsorbate:

$$Z = n/M \quad (2.4)$$

The rate of adsorption then can be defined as $K_a P(1-Z)$, where K_a is an adsorption rate coefficient, P is the pressure of the gas, and $(1-Z)$ is the fraction of unoccupied sites. At equilibrium, this rate must equal the rate of desorption, $k_d Z$.

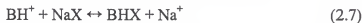
$$k_d Z = K_a P(1-Z) \quad (2.5)$$

Dividing the right side of this equation by k_d and setting $K_a/k_d = k$ leads to the familiar form of the equation:

$$Z = \frac{kP}{1 + kP} \quad (2.6)$$

In this form, k represents the ratio of adsorption to desorption rate coefficients, and is proportional to the bonding energy.

A similar derivation can be applied to simple binary ion exchange for the protonated species of organic bases on, for example, Na-montmorillonite:



where NaX and BHX represent the sorbed cations. The equilibrium expression for this reaction is:

$$K_{ie} = \frac{(BHX)(Na^+)}{(NaX)(BH^+)} \quad (2.8)$$

where K_{ie} is the exchange coefficient and parentheses denote activities. In many cases for homovalent exchange, concentrations can be used in place of activities since the activity

coefficients in the numerator and denominator virtually cancel each other for ions of the same valence (Harter and Baker, 1977). This yields:

$$K_{ie} = \frac{[BHX] [Na^+]}{[NaX] [BH^+]} \quad (2.9)$$

where the brackets denote concentrations in units of mmol/kg. Total charge on the exchanger can be expressed by the CEC, which is equal to $[BHX] + [NaX]$ in units of mmol/kg. Thus, equation 2.9 can be written in terms of the sorbed base species alone:

$$K_{ie} = \frac{[BHX] [Na^+]}{[BH^+] [CEC - [BHX]]} \quad (2.10)$$

Solving for the adsorbed cation concentration, $[BHX]$, and assuming $k_L = K_{ie}/Na^+$ yields,

$$[BHX] = \frac{CEC k_L [BH^+]}{1 + k_L [BH^+]} \quad (2.11)$$

Equation 2.11 is equivalent to the Langmuir expression for the adsorbed quantity of a protonated base as a function of solution concentration.

An associated Langmuir equation also can be derived from kinetic considerations. Assuming a chemical partitions between the solution (C) and the sorbent (S), then the rate at which cations sorb to the surface is:

$$\text{rate of sorption} = k_f C S_v \quad (2.12)$$

where k_f is the rate coefficient for sorption, C is the concentration of the chemical in solution, and S_v is the number of vacant sites. Alternatively, the rate at which ions desorb from the surface is:

$$\text{rate of desorption} = k_b S_o \quad (2.13)$$

where k_b is the desorption rate coefficient and S_o indicates occupied sites on the adsorbent. At equilibrium the rates of sorption and desorption are equal and,

$$k_f C S_v = k_b S_o \quad (2.14)$$

Assuming that the total number of sites is represented by S_{\max} , then the fraction of occupied sites can be represented as,

$$\frac{S_o}{S_{\max}} = \frac{b C}{1 + b C} \quad (2.15)$$

Where $b = k_f/k_b$, or the ratio of the sorption to the desorption rate coefficient.

In either case, the isotherm predicts that, for low concentrations of the adsorbate, the relationship will be linear while, at higher concentrations, a sorption maximum represented by the CEC is approached. CEC values, however, are dependent upon the method and the adsorbate employed for their determination, and adsorption maxima for organic cations frequently do not correspond to the CEC values determined from exchange of inorganic cations. Also, regression of the linearized form of the Langmuir equation often yields an adsorption maximum that is less than the CEC (Harter and Baker, 1977). Therefore, the actual adsorption maximum (S_{\max}) for the chemical of interest may need to be substituted for the experimental CEC in the equation.

There has been considerable debate over application of the Langmuir equation for adsorption of cations at colloid surfaces (Harter and Smith, 1981; Sposito, 1979; Harter and Baker, 1977). Most argument centers on the fundamental assumptions underlying development of the equation for exchange, and on the isotherm's subsequent use in assessing the relative affinities of adsorption for exchanging cations (Sposito, 1979). The essential assumptions are:

- 1) Adsorption sites must be covered by a monolayers at all times by one or both of the exchanging cations.
- 2) Adsorption sites must be uniform.
- 3) Adsorbed ions do not interact.
- 4) The exchange process must be reversible and one-for-one.

It is apparent that many of these assumptions may not be valid even in relatively simple clay-water systems. However, even among its most energetic detractors, it is conceded that the Langmuir equation is a good empirical isotherm for describing adsorption by many clay or soil systems (Harter and Smith, 1981). Thus, the Langmuir expression has been applied successfully to the sorption of a number of organic cations (El-Nahhal et al., 2001; Chen et al., 1999; Inel and Askin, 1996; Jaynes and Boyd, 1991; Narrine and Guy, 1981). It will be applied in the present context to sorption of the cationic form of those N-heterocycles to be studied.

The Linear Isotherm

The linear relationship is the oldest and simplest sorption isotherm, and is a special case of the Freundlich isotherm equation for $N=1$. It assumes direct proportionality between sorbed and solution constituents. It can be expressed by:

$$S = k_d C. \quad (2.12)$$

where k_d is a distribution coefficient indicating the relative amounts of a solute in solution (C) and sorbed to the soil matrix (S). Clay minerals have relatively low affinities for uncharged, non-polar organic molecules, and competition with water associated with adsorbed inorganic cations also severely limits sorption. Therefore, organic carbon existing as discrete particles or bound to mineral surfaces constitutes the primary sorptive phase for neutral organics. Therefore, the presence of organic carbon coatings or particles in soils and sediments has the potential to strongly impact organic base sorption (Banwart et al., 1982). Consequently, equation 2.12 can be modified to account for sorption solely on the organic fraction such that k_d/f_{oc} equals an organic carbon partitioning coefficient, K_{oc} (where f_{oc} =fraction of organic carbon in the sorbent). Thus:

$$S = K_{oc} f_{oc} C. \quad (2.13)$$

with K_{oc} values for organic compounds being routinely estimated from either the solubility or the octanol/water partitioning coefficient. A linear isotherm will be used to describe sorption of the neutral species of NHCs.

The Combined Isotherm

Linear combination of equations 2.11 and 2.13 yields a “combined isotherm” which integrates sorption of both species subject to their relative abundance in solution as dictated by pH (eq. 2.14):

$$S_T = \frac{CEC k_L (BH^+)}{1 + k_L (BH^+)} + K_{oc} f_{oc} (B) \quad (2.14)$$

where S_T is total sorption (umol/g), BH^+ (umol/g) is the protonated form of the nitrogenous base, and B (umol/g) is the neutral form. Based on the acid dissociation constant (K_a) of the NHC, the concentration of the neutral and protonated forms can be expressed as,

$$(BH^+) = \frac{B_T}{1 + 10^{(pH - pK_a)}} \quad (B) = \frac{B_T}{1 + 10^{(pK_a - pH)}}$$

At a pH approximately 2 units below or above the solute's pK_a value, eq. 2.14 can produce either Langmuir or linear isotherms, respectively. At intermediate pH values, where both components of sorption are active, the combined isotherm is L-type and resembles the Freundlich isotherm.

Equation 2.14 possesses an advantage over the Freundlich relation in that the combined isotherm incorporates a rudimentary theoretical framework to produce the frequently observed L-type isotherm common to many reported data. Fig. 2.2 illustrates a hypothetical combined isotherm for a compound having a pK_a of 6, CEC of 150 umol/g,

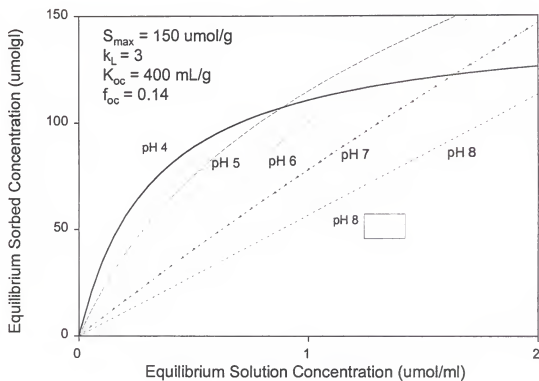


Figure 2.2. Hypothetical combined isotherm for quinoline at pH values between 4 and 8.

a K_{oc} of 400, a k_L of 3, and an f_{oc} of 14 g/g. The pH was incremented in this case from 4 to 8, and all other components in the equation were held constant between individual curves. Therefore, pH dictated the proportion, but not the total solute concentration in solution, while all other variables were held constant. As pH approaches the compound's pK_a value, the isotherm approximates a Freundlich isotherm.

The combined isotherm therefore permits an alternative approach to sorption of both NHC species that is consistent in form with the majority of reported data. Further, the approach is also more informative mechanistically than the Freundlich relation alone, since three of the four model parameters (CEC, K_{oc} , and f_{oc}) can be determined by independent means and are related to pertinent sorbent or sorbate properties. Cation exchange capacity and the fraction of organic carbon are routinely measured soil properties and, as stated, K_{oc} can be approximated from either solubility relationships or octanol/water partitioning coefficients (Karickhoff, 1981).

The single model parameter that cannot be easily determined is k_L . As described in the derivation of the Langmuir equation above, the analogous Langmuir coefficient k (eq. 2.6) is proportional to the bonding energy of the solute. However, this interpretation likely is not completely valid for aqueous solutions in contact with a diversely charged solid, since this type of system does not conform to many of the required model assumptions. Therefore, the parameter k_L must be either estimated by an alternative independent means, or optimized for a particular system.

Both methods will be employed here. For initial examination of the combined isotherm, k_L will be determined (i.e., calibrated) at low pH on a highly controlled sorbent

(organoclay). The resulting value then will be applied in the combined isotherm to describe sorption at other levels of pH on the same sorbent.

The parameter also will be optimized in the combined isotherm to obtain best simulations of experimental data for these model sorbents as well as for soils. There is no practical alternative to optimization for soils, since pH adjustment can strongly impact soil properties, rendering a measure of k_L values at low pH essentially meaningless at other levels of pH. Nonetheless, as a fitted parameter, the magnitude of k_L also should prove revealing.

It is important to note that the optimization procedure will determine only the magnitude of k_L , and will not affect the contribution of the neutral species to sorption. K_{oc} and f_{oc} will be held constant in the equation, regardless of pH. Thus, the fraction of total sorption ascribed to the neutral species will be known *before* the optimization. Consequently, an additional advantage of the combined isotherm is that it can be broken down into its two components to indicate the magnitude of sorption for each base species. For example, Fig 2.3 illustrates a hypothetical case for quinoline sorption at pH 5 (which is equal to the pK_a value) on a soil with a CEC of 10 $\mu\text{mol/g}$ and an organic carbon content of 1%. The two dashed lines indicate the individual contributions of each quinoline species.

This hypothetical case is typical of NHC sorption on a sorbent containing significant organic carbon relative to the CEC, with the comparative abundance of the two sorbent components being an important consideration. As discussed, the high selectivity for organic cations on soil colloids tends to overwhelm contributions to total sorption from the neutral species. Typically, however, the observation of dominant cation

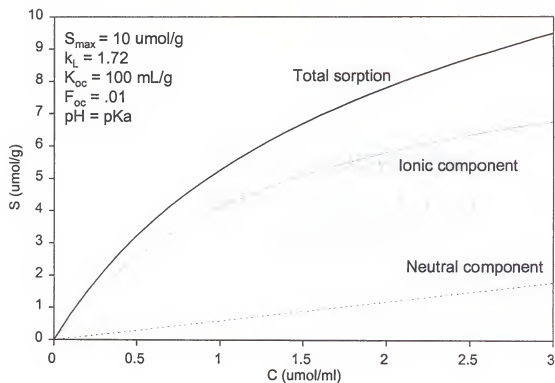


Figure 2.3. Hypothetical combined isotherm contributions to sorption by the neutral and protonated species.

sorption may be incorrectly assumed to indicate that the *absolute magnitude* of neutral-species sorption is therefore, insignificant. However, it is possible that merely the *relative* contribution of the neutral species is difficult to discern in a system that contains substantial cation exchange capacity. The combined isotherm however, can be dissembled or broken down into its component elements, permitting determination of the role of the neutral species however large or small.

Organoclays

To initially evaluate the relative or combined influences of cation exchange and hydrophobic partitioning, and to study application of the combined isotherm, organoclays were employed. Organoclays can be synthesized from the exchange of resident metallic cations on clay surfaces by organic alkylammonium cations. Replacement of hydrated alkaline or alkaline earth cations strongly enhances hydrophobicity of the clay interlayers, making them excellent sorbents for neutral hydrophobic compounds (Boyd et al., 1988; Jaynes and Boyd, 1990). Thus, organoclays have been proposed as components in a variety of waste containment barriers to inhibit the migration of toxic organic contaminants.

Organoclays are characterized as either *adsorptive* or *organophilic*, depending upon the size of the alkyl substituents on the organocations and the nature of their interaction with neutral hydrophobic compounds. Adsorptive clays result from exchange with quaternary ammonium ions of the general form $[(CH_3)_3NR]^+$, where R represents a relatively short hydrocarbon substituent group. Due to their relatively small size, these cations function as props or "pillars" in the interlamellar region, exposing siloxane surfaces to direct interaction with neutral hydrophobic compounds (Fig. 2.4).

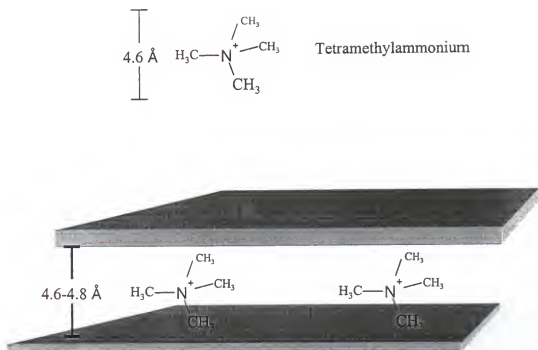


Figure. 2.4. Tetramethylammonium on a montmorillonite surface.

For example, tetramethylammonium and trimethylphenylammonium cations are shown to exist as discrete species on clay surfaces and to promote basal spacing of clay interlayers consistent with their size (Jaynes and Boyd, 1990). Uptake of neutral organics such as benzene or toluene by these clays also suggests that surface charge density is a determining factor in sorption, since the distance between charged sites ultimately will determine the degree of exposure of the clay surface.

Organophilic clays are produced from exchange with relatively long-chain alkylammonium cations ($R \geq 12$) which, upon adsorption, can form a hydrophobic partition medium within the clay interlayer. They can then function in a manner similar to a bulk organic phase such as octanol or hexane. The conformation and, thus, the ultimate sorptive characteristics of this interlayer partition phase are strongly dependent on the size of the alkyl substituent, particularly in relation to the charge density of the clay. Fig 2.5 shows some potential interlayer conformations of hexadecyltrimethylammonium (HDTMA) on four clays of differing charge density. Essentially, conformation is determined by the degree of close fit imposed on the alkylammonium cations based on clay charge density. Fully exchanged HDTMA smectites generally possess a bilayer configuration.

To create either species of organoclay, exchange with alkylammonium cations ordinarily is taken to completion, resulting in total coverage of the exchange complex to facilitate maximum sorption of hydrophobic organic compounds. HDTMA smectites, for example, can be perhaps 10-30 times more effective than soil organic carbon in the partitioning of neutral hydrophobic compounds (Nzengung et al., 1996; Lee et al., 1989; Boyd et al., 1988). In the present case, however, exchange will be allowed to take place

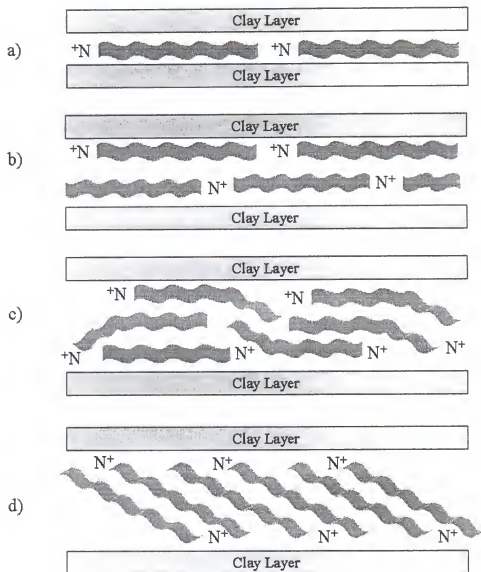


Figure 2.5. Potential configurations of interlayer cations (after Lagaly, 1982): (a) monolayer (1.37 nm), (b) bilayer (1.77 nm), (c) pseudotri-molecular (2.17 nm), (d) paraffin complex (>2.2 nm).

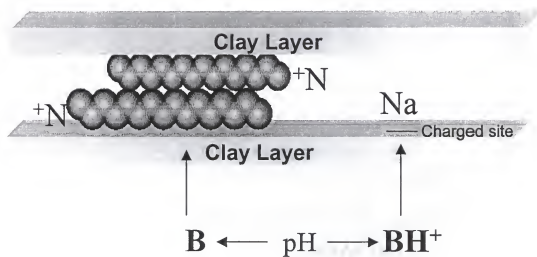


Fig. 2.6. Schematized sorbent domains for partially-exchanged organoclays.

at fractional levels of the CEC to create sorbents with a range of properties relative to the CEC and organic carbon content. The objective is to promote sorption of both species of organic base within separate, well-characterized, pH-independent sorbent domains. Fig 2.6 is a representation of the envisioned segregation of the two base species into separate organoclay domains; it is not meant to indicate the actual make-up of fractionally-exchanged interlayers. This issue will be comprehensively discussed in a later chapter.

Based on preliminary work that also will be discussed, clays were exchanged at levels between 20% and 200% of the CEC. Characteristics of these organoclays, to be discussed in Chapter 3, indicated that sorption of NHCs and application of the combined isotherm could best be examined with clays exchanged at levels 60%, 80%, and 100% of the CEC.

Experimental Organization

NHC sorption to a variety of sorbents under a number of conditions will be discussed in the following three chapters. Chapter 3 details the synthesis and characterization of organoclays. It primarily describes the intercalation of HDTMA cations in the clay interlayer and the impact of HDTMA arrangement on the sorption of neutral molecules. Chapter 4 examines sorption of the nitrogen heterocycle, quinoline, on selected organoclays. Quinoline was chosen as a probe sorbent to determine the essential sorption characteristics of NHCs in general. Quinoline is moderately soluble, moderately hydrophobic, and has a pK_a of 4.92, and should sorb in a manner that is mechanistically similar to many NHCs. Chapter 5 initially examines the sorption of quinoline on soils. Subsequently, quinoline behavior is compared with that of 2-methylpyridine and acridine.

CHAPTER 3
MONOLAYER TO BILAYER TRANSITIONAL ARRANGEMENTS OF
HEXADECYLTRIMETHYLAMMONIUM CATIONS ON SODIUM-
MONTMORILLONITE

Introduction

Organoclays are synthesized from the exchange of resident metallic cations on clay surfaces by organic alkylammonium cations. Replacement of hydrated alkaline or alkaline earth cations strongly enhances the hydrophobicity of the clay interlayers, making them excellent sorbents for neutral hydrophobic compounds (Jaynes and Boyd, 1991; Boyd et al., 1988). Thus, organoclays have been proposed as components in a variety of waste containment barriers to inhibit the migration of toxic organic contaminants.

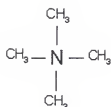
Organoclays are characterized as either adsorptive or organophilic, depending upon the size of the alkyl substituents on the organocations and the nature of their interaction with neutral hydrophobic compounds. Adsorptive clays result from exchange with quaternary ammonium ions of the general form $[(CH_3)_3NR]^+$, where R represents a relatively short hydrocarbon substituent group. Due to their relatively small size, these cations function as props or "pillars" in the interlamellar region, exposing siloxane surfaces to direct interaction with neutral hydrophobic compounds. Organophilic clays are produced from exchange with relatively long-chain alkylammonium cations ($R \geq 12$), which, upon adsorption, can form a hydrophobic partition medium within the clay interlayer, and function analogously to a bulk organic phase such as octanol or hexane. The conformation and, thus, the ultimate sorptive characteristics of this interlayer partition phase are strongly dependent on the size of the alkyl

substituent, particularly in relation to the charge density of the clay. Some typical alkylammonium cations used in the synthesis of both types of organoclays are shown in Fig. 3.1.

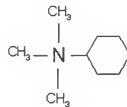
To create either species of organoclay, exchange with the alkylammonium cation ordinarily is taken to completion, resulting in total coverage of the exchange complex to facilitate maximum sorption of hydrophobic organic compounds. The amount of exchange, however, can be tailored to specific objectives. For instance, it has been shown that clays partially exchanged with hexadecyltrimethylammonium (HDTMA) cations can maintain an organophilic character in proportion with their fractional coverage of the exchange complex, within certain limits (Boyd et al., 1988). The physical arrangement of the organic cation within the interlayers at fractional coverage—which, in part, determines these limits—is however, less well understood.

The majority of work related to the conformation of adsorbed interlayer alkylammonium cations has focused on relatively short-chain varieties like trimethylammonium (TMA), trimethylphenylammonium (TPMA), or a number of primary to quaternary amines (Jaynes and Boyd, 1990; Lee et al., 1989; McBride and Mortland, 1975; Theng et al., 1967). At maximum adsorption on smectite clays, these organocations are arranged in monolayers. At fractional levels of adsorption, however, the organic and metallic cations tend to segregate into randomly interstratified layers dominated by a single species.

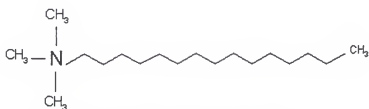
McBride and Mortland (1975) reported that, below about 55% of the CEC, both TMA and TPMA organo-smectites exhibit random interstratification of interlayers dominated by either organic or metallic (e.g. Cu^{2+}) cations. At greater loadings up to 100%



Tetramethylammonia (TMA)



Trimethylphenylammonia (TMPA)



Hexadecyltrimethylammonia (HDTMA)

Figure 3.1 Three types of alkylammonium cations used in the synthesis of organoclays

coverage, however, basal spacings in these clays maintained a single value that was indicative of organic monolayers with no evidence of interstratification. This suggests that the organic and metallic cations coexisted in the same interlayers, and that basal spacings were fixed by the alkylammonium ion. Further, when clays exchanged to between 55% and 100% of the CEC were equilibrated at two levels of hydration there was a fairly constant difference in interlayer spacing. This implies that interlayer hydration (presumably due to Cu^{2+}) still could impact d-spacing, and that the effect was not necessarily dependent on the absolute amount of Cu^{2+} in the system, but merely upon its presence. Some elasticity of interlayer spacings for moist and oven-dried primary to quarternary adsorptive clays also was noted by Theng et al. (1967).

Less is known about the nature and conformation of intercalated long-chain alkylammonium cations on partially-exchanged organophilic clays. Depending on the charge density of the clay and the fraction of the CEC occupied, long-chain alkylammonium cations conceivably can adopt monolayer, bilayer, pseudotrimolecular, or paraffin type arrangements (Fig. 3.2). Boyd et al. (1988) reported basal spacings consistent with random interstratification of Ca^{2+} and bilayer HDTMA interlayers for partially-exchanged montmorillonite. However, exchange was performed at only three levels—35%, 70%, and 100% of the CEC. Alternatively, transitional monolayer-to-bilayer arrangements have been reported for high-charge smectites (Lagaly, 1982; Lagaly et al., 1976).

The purpose of the present study was to examine intercalation of HDTMA cations on a typical low-charge Na-smectite (Swy-2) in order to determine the nature of adsorption and the ionic composition of the interlamellar region. Clays were exchanged at levels between

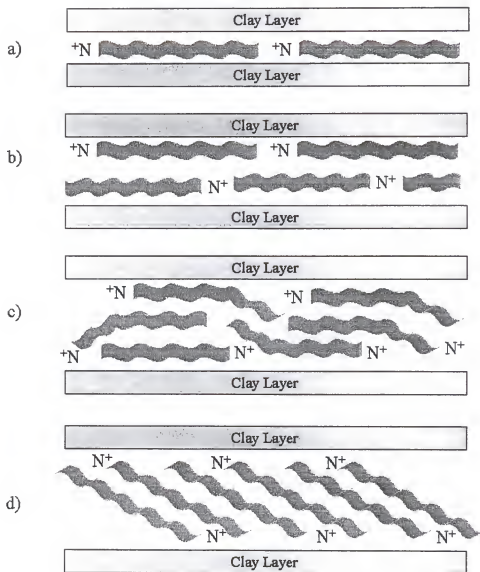


Figure 3.2. Potential configurations of interlayer cations (after Lagaly, 1982):
 (a) monolayer (1.37 nm), (b) bilayer (1.77 nm), (c) pseudotri-molecular (2.17 nm), (d) paraffin complex (>2.2 nm).

20% and 200% of the CEC, and basal spacings were determined at two relative humidities. The effect of hydration lent additional insight into the makeup and properties of the interlayer volume that otherwise could not be determined. The migration of water into the interlayer established the role and location of Na^+ remaining on the exchange complex following adsorption of varying levels of HDTMA. The sorption of naphthalene, a neutral hydrophobic compound, was employed to determine the analogous properties of the organic phase.

Materials and Methods

Materials

Na-montmorillonite (Swy-2) was obtained from the Source Clay Repository of the Clay Minerals Society (Colombia, MO). Reagent grade hexadecyltrimethylammonium chloride and naphthalene were obtained from Fisher Scientific (Pittsburgh, PA). Naphthalene is a weakly soluble (31.7 mg/l), neutral, hydrophobic ($\log K_{ow} = 3.37$) compound, which exhibits linear sorption on HDTMA montmorillonites at levels below about 20% of its solubility (Nzengung et al., 1996; Jaynes and Boyd, 1991). Sorption is believed to be characterized by hydrophobic partitioning of the sorbate into the organic phase created by HDTMA, since naphthalene has little affinity for Na-montmorillonite. It is useful, there, as a probe compound for assessment of the organophilic character of partially- and fully-exchanged clays.

Preparation of Organoclays

Organoclays were prepared from the wet-sedimented fraction obtained from the specimen clay as described by Nzengung et al. (1996). The $< 2\mu\text{m}$ fraction was washed 3

times with a 0.1 M NaCl solution, and then washed twice with 0.05 M NaCl followed by a final wash with deionized water. The CEC of the resultant Na-montmorillonite was determined by ^{45}Ca exchange at a measured pH of 6.0, and was equal to 819 mmol(+)/kg. Na-clay suspensions containing 2 g of clay were treated with solutions containing HDTMA equal to the desired fractional coverage of the CEC (20, 40, 60, 70, 80, 90, 100, 150, and 200%) and allowed to incubate overnight. The resulting organoclays then were centrifuged, washed thoroughly, and freeze-dried. Organic carbon contents of the organoclays were calculated from the amount of HDTMA adsorbed at each level. Adsorbed HDTMA was determined as the difference between the amount initially in solution, and that remaining following equilibration. The clays were stored in a dessicator over P_2O_5 until used.

X-ray Analysis

Dried organoclays deposited on low-background quartz crystal XRD mounts were equilibrated over a large quantity of a saturated CaCl_2 solution in a desiccator to establish the relative humidity at 40%. To ensure constant humidity during the analysis, a constant-humidity "chamber" with a Mylar window for beam passage was constructed around the diffractometer stage, and fitted with a digital hygrometer (Harris et al., 1992). Triplicate X-ray scans were made between $40 \pm 2\%$ relative humidity and $97 \pm 1\%$ relative humidity. Small differences in the thickness of the mounts, as well as swelling of the mounts due to hydration, changed the angle of the beam relative to the sample. Therefore, corrections were made in the diffraction peaks, when necessary, based on the known position of a slight quartz peak that was observed in each sample. Samples were scanned at $2^\circ 2-\Theta$ per min using $\text{CuK}\alpha$ radiation.

Naphthalene Sorption

Equilibrium sorption of naphthalene from aqueous solution on all clays was examined using a stirred batch method at a single initial concentration of 5 mg/L (Nkedi-Kizza et al., 1985) with a solution:clay ratio of 100:1. Clay was weighed into 15 ml glass centrifuge tubes and the naphthalene solutions were added. The tubes then were shaken at ambient temperature (25°C) for 24 hours (Nzengung et al., 1996), and equilibrium solutions were obtained by centrifugation at 1200 g for 15 min. Naphthalene concentrations were determined by High Performance Liquid Chromatography (HPLC) using ultraviolet detection, a C-18 column, and a 60:40 acetonitrile:water mobile phase. Sorbed naphthalene was determined as the difference between the amount added to each tube and that remaining in the equilibrium solution. The sorption coefficient, K_d , was computed from the equation $S = K_d C$, where S is the amount of naphthalene sorbed to the clay (mg/g), and C is the equilibrium solution concentration of naphthalene (mg/mL).

Results and Discussion

Basal Spacings at Low Relative Humidity

HDTMA cations typically take up a bilayer configuration in low-charge smectites at 100% coverage of the CEC. Evidence of interstratification of these bilayers with Na^+ interlayers has been reported for clays partially exchanged with HDTMA (Boyd et al., 1988), but basal spacings from progressive coverage of Na-montmorillonite by HDTMA in the present investigation could not be reconciled with a construct based upon segregated, randomly interstratified, sodium and HDTMA interlayers. Basal spacings in such a case necessarily would reflect the proportions of the interlayers exclusively occupied by each

cation. In effect, with each increment of coverage, HDTMA would occupy progressively greater numbers of randomly distributed interlayers, increasing the resultant d-spacings accordingly. The present data suggest that HDTMA assumed two dominant configurations within the interlayer at low (<70%) and high (>70%) coverages (Fig. 3.3). Between 20% and 60% coverage, the magnitude and relative constancy of d_{001} suggest that HDTMA and sodium exist within the same interlayers, and basal spacing was governed largely by monolayer coverage of the alkylammonium cation. In other words, there was no evidence for significant random interstratification of homogeneous Na^+ and HDTMA layers. Measured d-spacings were somewhat greater than the 1.34 nm calculated for monolayer HDTMA-smectite given silicate sheet and alkyl chain thicknesses of 0.94 nm and 0.40 nm, respectively. Basal spacings were also greater than those observed previously for dehydrated, fully-exchanged monolayer n-alkylammonium-montmorillonite samples (Laird et al., 1989). However, water was not excluded from the interlayer, in the present case, which remained relatively hydrophilic at low HDTMA loadings. This could cause the alkylammonium carbon tails to gravitate away from the Na- and water-populated surface to produce the measured spacings.

Exchange beyond 60% evidenced a developing bilayer arrangement for HDTMA, terminating at the characteristic d-spacing of ≈ 1.77 nm for a nominal 100% coverage (Nzengung et al., 1996; Lagaly et al., 1976; Theng et al., 1967). A transition between the two principal arrangements also was indicated (Fig. 3.4). Initialization of the transition to a bilayer configuration is observable as a low-angle peak broadening for the 60% organoclay, which suggests the incipient development of a bilayer phase. An increase in the position of the

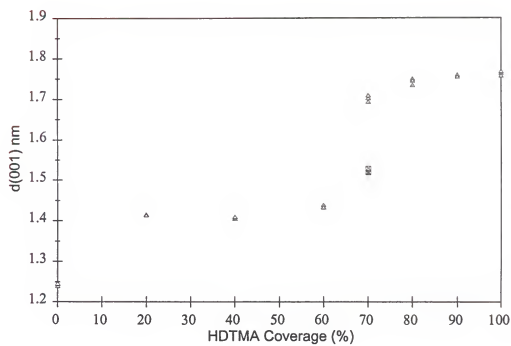


Figure 3.3. Basal spacings for organoclays at low relative humidity.

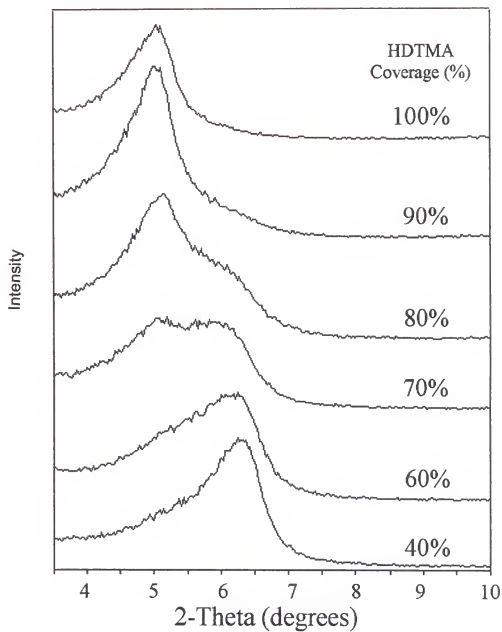


Figure 3.4. X-ray diffractograms for six organoclay coverages.

primary peak to 1.47 nm also suggests some potential random interstratification of the two principal phases, as do the two peaks of relatively equal intensity at 70% coverage. Neither of these peaks precisely corresponds to the monolayer or the bilayer spacings. The peaks instead appear to be shifted toward an intermediate position between the two. With still greater HDTMA loading between 80% and 100% coverage of the CEC, the dominant arrangement appeared to be bilayer. However, weak, high-angle "shoulders" on both peaks which roughly correspond to the monolayer d-spacing suggested that some residual monolayer phases persisted. Not until 100% coverage did the diffraction peak resolve to a single, discrete peak at 1.77 nm. This is indicative of an exclusively bilayer arrangement.

The overall transition may reflect the adsorption characteristics of HDTMA. At low surface loadings, the adsorption process is driven primarily by electrostatics augmented by van der Waals interactions of the carbonaceous alkyl chains with siloxane surfaces. With increased loadings, however, adsorption shifts to a more dominantly hydrophobic process involving associations between the alkyl chains of resident and incoming cations. This fundamental change in sorption character, and the resultant reorientation of interlayer cations, ordinarily is attributed to steric constraints. These, in turn, are dictated by the relative planar areas of the alkylammonium cations and the configuration of charged sites on the smectite surface in an interlayer volume fully occupied by alkylammonium cations (Olis et al., 1990; Stul and Mortier, 1974). When the area of the alkylammonium cation exceeds the area available per charged site, the ions are obliged to assume an alternative configuration within the interlayer.

Basal spacings at still greater coverages equal to 150% and 200% of the CEC increased to 1.86 nm and 2.08 nm, respectively. At these levels of HDTMA uptake, sorption likely was

driven solely by hydrophobic interactions among carbonaceous portions of the HDTMA cations. Accommodation of the organic cation in the uncharged, strongly hydrophobic interlayer space—which would cause such expansion—is difficult to envision. However, although the cation remains charged, it may not be sufficiently hydrated to obviate the potentially powerful interactions among the aliphatic portions of the adsorbed species. Further, charged alkylammonium cation heads can protrude from the interlayer space at high adsorption levels. The increase in d_{001} , therefore, may be due to swelling of the interlayers in a manner similar to that documented for the absorption of organic solvents by HDTMA organoclays (Nzengung et al., 1996), rather than a conformational shift. Adsorption beyond the CEC also may have involved HDTMA-chloride ion pairs, or aggregation of organic cations at the clay surface (Rytwo et al., 1991). Interaction of the carbon chain with adsorbed HDTMA on external surfaces or crystal edges also is conceivable, but should not lead to increased d-spacings.

Overall, the data demonstrate that the orientation of interlayer cations is contingent upon both their absolute numbers and their density, in conjunction with their planar areas relative to those of the charged sites on montmorillonite. In effect, there first must be sufficient numbers of the alkylammonium cations to support the formation of a bilayer; and, second, their density must exceed a critical level to induce reorientation to their ultimate bilayer configuration.

Hydration of Clay Interlayers

Hydration of the organoclays provided additional clues to the potential makeup of the interlayer volume with Fig 3.5 demonstrating the change in d-spacing with clay hydration. The

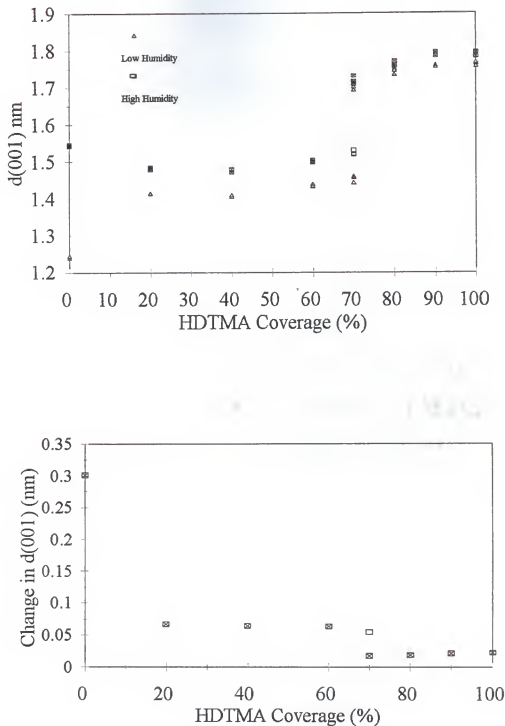


Figure 3.5. Basal spacings of partially-exchanged organoclays at two relative humidities (a), and the change in d -spacing with hydration (b).

impact of hydration was uniform within the ranges of predominance for monolayer and bilayer coverage, suggesting that overall ordering of sodium and HDTMA within the interlayers remained similar although the relative proportions of each cation did not. Sodium ions are responsible for interlayer expansion due to hydration at low HDTMA coverages. Thus, given almost uniform response to hydration, expansion of the interlayers depended on merely the presence rather than the amount of interlayer sodium. Further, water apparently was able to migrate unimpeded into the interlayer space, regardless of coverage. This suggests pervasive, contiguous domains of sodium within the interlayers. In essence, the two “phases”, dominated by either HDTMA or sodium, although not segregated into discrete interlayers, nonetheless functioned independently.

Beyond 60% coverage, clay expansibility decreased in conjunction with the apparent change in configuration, rather than the amount, of HDTMA in the interlayers. The almost uniform response to hydration above 60% exchange also suggests that expansion was dictated by a similar mechanism among these higher-coverage clays. The source of this interlayer expansion is uncertain. The structure of water in an interlayer partially occupied by organic cations is not known and, thus, its impact on interlayer expansion is unpredictable. The expansion did not depend strongly on the relative amounts of metallic or organic cations on the exchange sites, so it appears that expansibility upon hydration was controlled by either one cation or the other. If sodium hydration dictated the expansion, then the structure of water molecules was fundamentally different than for lower HDTMA coverages. For example, with 80% coverage, d-spacing increased from 1.74 nm to 1.76 nm upon hydration. However, the basal spacing for the hydrated, fully-expanded Na^+ interlayer was only 1.54 nm and, thus, too

small to yield the observed spacings. A possible alternative explanation may be that hydration of HDTMA itself caused the interlayer expansion. The aliphatic hydrocarbon "tail" of HDTMA is hydrophobic (Fig. 3.1), but the polar nitrogen "head" admits the potential for hydration and consequent expansion of the interlayers.

Naphthalene Sorption

It is apparent that, below full saturation of the exchange complex with HDTMA, the majority of organic and metallic cations do not segregate into discrete interlayers as has been demonstrated for short-chain alkylammonium cations (McBride and Mortland, 1975; Mortland, 1970). However, indirect observations of the access of water to polar regions in the interlayer space of partially-exchanged clays (discussed above) as well as the separation of the interlayers themselves, suggest that they *do* tend to segregate within the same interlayers and largely function independently with respect to water. This begs the question of whether organic compounds can access the organic domains as readily.

Sorption of naphthalene to the partially-exchanged clays provided an affirmative, although qualified, answer. Fig. 3.6 compares the partitioning coefficients (K_d) of naphthalene for all of the organoclays discussed above, based on organic carbon content. The straight line through the data was derived from linear regression of the K_d values for the 80%, 90%, and 100% coverages, where bilayers and consequently a more stable partitioning phase was better developed. Despite some potential sharing of the interlayer space between Na^+ and HDTMA, as suggested by hydration of the clays, K_d values were highly linear in this region.

Sorption appeared to decline with excess coverage by HDTMA in amounts equal to 150% and 200% of the CEC. Neutral hydrophobic compounds sorbed on HDTMA smectites

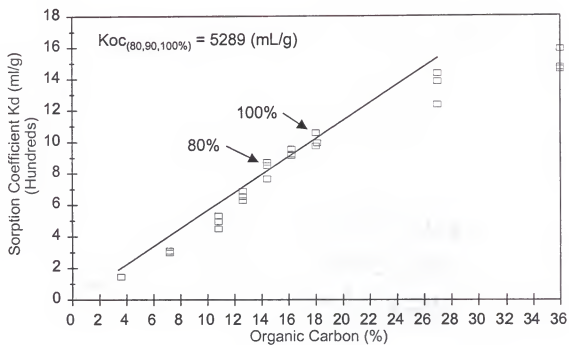


Fig 3.6. Naphthalene sorption on the full range of organoclays

tend to augment the sorptive capacity of organoclays for other, or the same neutral compounds (Sheng et al., 1996; Traina and Onken, 1991). However, polar or charged groups on alkylammonium cations which were sorbed beyond the CEC and thus were unbalanced by charges on the clay surface may have diminished the hydrophobic character of the interlayer. This could have limited the uptake of naphthalene.

Below 80% coverage, partitioning of naphthalene into the organic phase also appeared to decline. Either the monolayer conformation of the organic cations within the interlayer, or the presence of water and Na^+ in close proximity to the organic domains, may have reduced K_{oc} compared with values for organoclays dominated by bilayers. There was, however, a gradual increase in naphthalene sorption as HDTMA occupancy increased and bilayers began to develop. Thus, sorption to the 70% organoclays (at the midpoint of the transition between monolayers and bilayers) approached levels achieved for the 80%, 90%, and 100% organoclays.

Note that, while naphthalene sorption as indicated by K_{oc} declined below 80% coverage, expansion due to hydration was essentially uniform. Sorption thus appeared to be more susceptible to potential influences from the polar domains within the interlayer, which is consistent with the proposed composition of the interlayer. Expansion was not contingent upon hydration of *all* interlayer Na^+ ions, but K_{oc} values do derive from the number of interlayer HDTMA aliphatic substituents accessed, as well as their conformation. As coverage increased, potential interference with sorption from proximate hydrophilic domains within the same interlayer apparently declined.

Conclusions

Overall, results from both x-ray analysis and sorption of naphthalene were internally consistent. Heterogeneous monolayers and bilayers with sodium dominated clay interlayers, depending upon surface coverage by HDTMA. However, despite this heterogeneity, Na^+ and HDTMA apparently occupy functionally discrete domains which are reflected by the clays' response to the sorption of naphthalene and to hydration.

Intercalation of the alkylammonium cations apparently was governed by fundamentally different processes at low and high surface coverages. Electrostatics augmented by van der Waals interactions of the alkyl hydrocarbon chains with siloxane surfaces apparently dictated adsorption at lower surface densities. At greater loadings, however, adsorption shifted to a more dominantly hydrophobic process involving associations between the alkyl chains of resident and incoming cations.

The true character of these processes might best be assessed with thermodynamic techniques, spectroscopy, or correlation of surface charge density with the planar area of a number of organic cations (or the number of carbon atoms in the alkyl substituents). Regardless of the particular technique, it is necessary to address the specific mechanisms and the adsorbate or adsorbent properties controlling the conformation and distribution of the interlayer cations.

CHAPTER 4 ORGANOCLAYS AS MODEL SORBENTS FOR QUINOLINE

Introduction

The organoclays discussed in Chapter 3 provide a unique medium for evaluating the sorption of ionizable organic compounds. Recall that organic bases in general, and N-heterocycles (NHCs) in particular, are distinguished by their ability to speciate in solution subject to pH. Neutral NHCs, by definition, contain nitrogen moieties capable of accepting protons and becoming positively charged. Thus, two fundamentally different mechanisms—adsorption of the cation and partitioning of the neutral species into organic carbon—determine overall sorption. Delineating these mechanisms in natural sorbents is problematic, however, since they are mutually and interdependently influenced by pH, sorbent composition, and chemical characteristics.

Fractionally and fully exchanged organoclays provide a measure of control over these influences. Sorbent components can be comparatively well defined, and, based on the results of chapter 3, apparently exist in discrete domains that are independently accessible to both polar and non-polar solution constituents. Thus, it is believed that the two organoclay domains can function independently in the uptake of each species of NHC and that relative sorption of the cation and the neutral molecule is dictated primarily by two factors: solution pH and the compound's pKa value for a given fractional coverage of the clay surface by HDTMA

To determine the relative magnitudes of sorption for each NHC species, the combined Langmuir-linear isotherm derived in Chapter 2 was employed. The combined isotherm is essentially a linear combination of the two isotherm equations that describe the dominant mechanisms that appear to be responsible for overall sorption of organic bases.

$$S_T = \frac{S_{\max} k_L (BH^+)}{(1 + k_L (BH^+))} + K_{oc} f_{oc} (B^0) \quad (4.1)$$

The first term in eq. 4.1 defines adsorption of the cation in terms of an H-type isotherm, and the second term describes linear partitioning of the neutral species between the solution and organic carbon. Here, BH^+ and B^0 are the respective concentrations of the two species of the organic base (in the present case, quinoline) in aqueous solution subject to pH for a given sorbent as described below:

$$(BH^+) = \frac{B_T}{1 + 10^{(pH-pK_a)}} \quad (B^0) = \frac{B_T}{1 + 10^{(pK_a-pH)}}$$

The parameters S_{\max} , K_{oc} , f_{oc} and k_L in equation 4.1 are constants, representing the sorption maximum, the organic carbon partitioning coefficient, the fraction of organic carbon on the sorbent, and an empirical coefficient, respectively. As discussed, the contribution of the neutral and protonated species to total sorption will be determined by disassembling eq. 4.1 into its two principal components.

Cation exchange is believed to be the primary mode of adsorption (Chapter 2). Therefore, the sorbent cation exchange capacity (CEC) for the present group of experiments was manipulated via fractional coverage of a Na-smectite by HDTMA cations at levels of 0, 60, 80, and 100% of the CEC. Exchange with HDTMA decreased the cation exchange capacity in proportion to an increase in the resultant fraction of organic carbon, f_{oc} . The total isotherm was contingent only upon the concentrations of the

two NHC species as dictated by pH, since S_{\max} , k_L and K_{oc} in eq. 4.1 will be held constant for each sorbent. The principal advantage of the combined isotherm is that the model coefficients are related to recognizable sorbent-sorbate parameters—specifically the CEC and organic carbon content of the sorbent—and the organic carbon partitioning coefficient of the sorbate.

Overview

Preliminary evaluation of the isotherm required isolation of the two proposed sorption mechanisms under conditions that rendered them mutually exclusive. Therefore, experiments initially were conducted at two extremes in pH and sorbent composition to yield isotherms at pH 3 on Na-clay, and pH 8 on HDTMA-saturated clay. In the former case, quinoline equilibration with Na-montmorillonite limited the primary interaction to adsorption/exchange; in the latter, sorption of the neutral quinoline molecule at pH 8 on the HDTMA organic phase confined the interaction to aqueous-organic partitioning.

Subsequent quinoline sorption trials at the same two levels of pH on two *fractionally exchanged* organoclays (60% and 80% exchange) removed the constraint of homogeneous sorbent composition, while preserving the limitation on compound speciation. The immediate goal was to determine if the presence of both sorbent domains in the presence of a single quinoline species would lead to substantial departures from the proposed isotherms comprising the two terms of the combined isotherm. Secondly, the experiments determined the coefficients S_{\max} , k_L , and K_{oc} for model evaluation at other levels of pH for the 60% and 80% organoclays.

The first two of these coefficients, S_{\max} and k_L , were determined by regression of the pH 3 data according to a linear form of the Langmuir expression:

$$\frac{C}{S} = \frac{1}{S_{\max} k_L} + \frac{C}{S_{\max}} \quad (4.2)$$

where S is the equilibrium concentration of adsorbed quinoline per unit mass of adsorbent ($\mu\text{mol/g}$). The remaining isotherm parameter, K_{oc} , was determined by linear regression of the pH 8 sorption data for each organoclay, and is equal to the slope of the regression line divided by the weight fraction of organic carbon. The effectiveness of the combined isotherm employing these coefficients ultimately was evaluated against the Freundlich equation, which is the most widely used isotherm for overall sorption of organic bases. Based on the outcome of these comparisons, the parameter k_L subsequently was optimized by non-linear least squares regression to improve the accuracy of the isotherm projections.

Materials and Methods

Materials

Na-montmorillonite (Swy-2) was obtained from the Source Clay Repository of the Clay Minerals Society (Colombia, MO). Reagent grade hexadecyltrimethylammonium chloride was obtained from Fisher Scientific (Pittsburgh, PA). Reagent-grade quinoline was obtained from Aldrich Chemical. Quinoline has a pK_a of 4.92 and an octanol-water partitioning coefficient of 102 ml/g (Zachara et al., 1990).

Preparation of Organoclays

Organoclays were prepared from the wet-sedimented fraction obtained from the specimen clay as described by Nzengung et al. (1996). The $< 3\mu\text{m}$ fraction was washed 3 times with a 0.1 M NaCl solution, rinsed twice with a 0.05 M NaCl solution and finally rinsed with deionized water. The CEC of the resultant Na-montmorillonite was determined by ^{45}Ca exchange at pH 6 (Appendix A), and was equal to 819 mmol(+)/kg.

Na-clay suspensions containing 20 g of clay were treated with solutions containing HDTMA equal to the desired coverage of the CEC (60, 80, and 100%) and allowed to incubate overnight, shaking continuously. The resulting organoclays were then centrifuged, washed, and freeze-dried. CEC values for the fractionally exchanged clays were determined by ^{45}Ca exchange, and organic carbon contents of the organoclays were calculated from the amount of HDTMA adsorbed at each level. Total carbon of the organoclays also was determined from combustion, with subsequent measurement of CO_2 evolved. The clays were stored in a desiccator over P_2O_5 until used.

Quinoline Sorption

Equilibrium sorption of quinoline from aqueous solution on all clays was examined using a stirred batch method (Nkedi-Kizza et al., 1985) with a solution:clay ratio was 300:1. Initial quinoline solution concentrations ranged between 0.25 $\mu\text{mol/mL}$ and 4.40 $\mu\text{mol/mL}$ in 0.02 M NaCl. The pH was adjusted through addition of either HCl or NaOH. Clay was weighed into 30-ml polypropylene centrifuge tubes and the appropriate aqueous quinoline solutions were added. The tubes then were agitated on a reciprocal shaker at ambient temperature (25°C) for 24 hours (Nzengung et al., 1996; Nkedi-Kizza et al., 1985). Equilibrium was reached within 8 hours. Samples of the equilibrium solutions were obtained from the supernatant following centrifugation. Quinoline concentrations were determined by High Performance Liquid Chromatography (HPLC) using ultraviolet detection ($\lambda=280\text{ nm}$), a C-18 column, and a 0.50 M ammonium acetate:methanol mobile phase in a ratio of 70:30. Sorbed quinoline was determined as the difference between the amounts initially added to each tube and that remaining in the equilibrium solution.

Results and Discussion

Isolation of Model Components on Na- and 100% HDTMA Clays

Initial results for quinoline sorption on the Na-clay and the 100% HDTMA clay at pH 3 and pH 8, respectively, indicated that each term in the combined isotherm equation was closely descriptive of the experimental data (Fig. 4.1). In other words, the fundamental assumptions relative to the application of the Langmuir and linear terms appeared to be appropriate within the present context. At pH 3, greater than 99% of the quinoline should be ionized, and it is evident that the exchange domains within the organoclays and initially occupied by Na^+ were accessible to the cation. Adsorption was well described by the Langmuir term of the isotherm, and is consistent with past observations for organic cations (Brown and Combs, 1984). At pH 8 on the fully exchanged organoclay, linear sorption was observed.

The figure also suggests the relative strengths of sorption for the neutral and protonated species of quinoline. At low solution concentrations, sorption of the cation is far stronger than absorption of the neutral species owing to high affinity for the protonated base at low clay surface loadings of quinolinium. At higher solution concentrations, this dominance declines as adsorption approaches S_{max} . Manifestly, in mixed sorbents containing both exchanger and organic domains, potential adsorption dominance naturally will depend on two factors in addition to pH: the solution concentration of quinoline, and the magnitude of the organic carbon content relative to the exchange capacity. This latter relation is integral to sorption of NHCs. Exchange affinity is characteristically higher than the strength of molecular absorption, frequently leading to neglect of the neutral species as a significant component to overall sorption. However, given sufficient organic carbon in relation to the exchange capacity, the natural

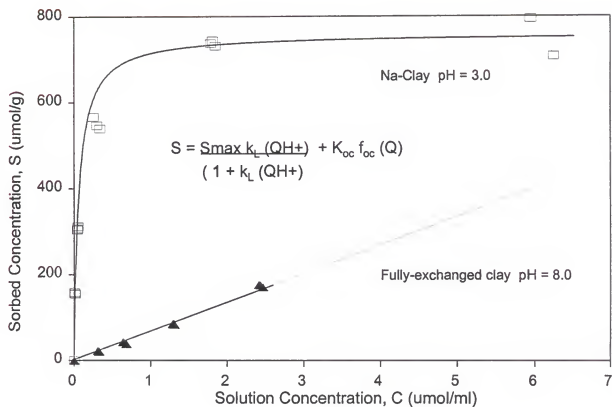


Figure 4.1. Sorption of quinoline on Na-clay and 100% HDTMA organoclay at pH 3.0 and pH 8.0.

dominance of cationic adsorption may be overcome, and the influence of the neutral species on the overall process made more evident.

Sorption on Fractionally-Exchanged Organoclays

The above experiments on Na- and fully exchanged HDTMA clays demonstrated the applicability of the Langmuir and linear terms in the combined isotherm to independent sorption of each species. Sorption on the *fractionally* exchanged clays at pH 3 and 8 were designed to test the models on mixed sorbents, and to determine the parameters S_{\max} , k_L , and K_{oc} for use in the model. These parameters then could be employed ultimately to describe sorption data on fractionally exchanged clays at *other* levels of pH.

Determination of S_{\max} and k_L for cation adsorption

Sorption of the cation at pH 3 on the 60 and 80% organoclays was well-described by the Langmuir term of the combined isotherm, and indicated that the magnitudes of the coefficients k_L and S_{\max} were unique to each sorbent. Fig. 4.2 compares three quinoline isotherms at pH 3, and demonstrates that both coefficients declined with increasing HDTMA coverage up to 80% of the CEC.

The decline in the sorption maximum with HDTMA coverage was a matter of course, but k_L customarily has been related to the affinity of the cation for the adsorbent (Harter, 1979; Shukla and Mittal, 1979; Harter and Baker, 1977). The potential implications of k_L as a sorption parameter will be discussed in a later section; however, the observed reduction in k_L with increasing HDTMA exchange suggests a consonant decrease in affinity that is inconsistent with one of the governing assumptions of the Langmuir equation, which dictate that all exchange sites possess equal energy. It appears,

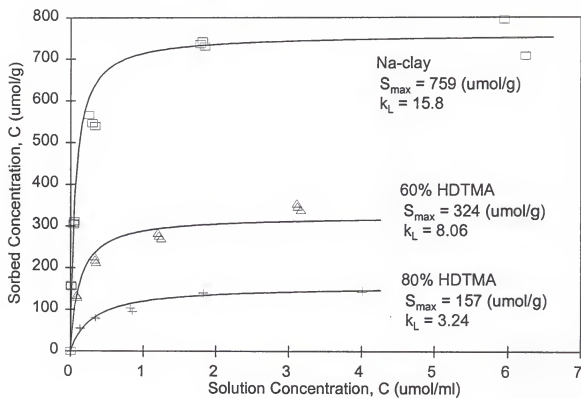


Figure 4.2. Quinoline sorption on Na- and 100% HDTMA clay at pH 3.0..

however, that adsorbed HDTMA cations may have occluded the most energetically-favorable exchange sites implying, *a priori*, their *non*-uniformity.

Determination of K_{oc} for neutral quinoline

Sorption of neutral quinoline at pH 8 was linear and well-correlated with the organic carbon content of the three organoclays (Fig. 4.3), supporting the assumption that the second term in the combined isotherm is governed by an aqueous-organic partitioning mechanism. K_{oc} values for the organoclays were essentially constant (avg. $K_{oc}=392.7$), although significantly greater than proposed K_{oc} values calculated from quinoline's octanol-water partitioning coefficient. Table 4.1 lists three K_{oc} values calculated from the literature based on compounds with a similar K_{ow} .

Table 4.1 Calculated K_{oc} values for quinoline.

<u>Source</u>	<u>K_{oc}</u>
Schwarzenbach and Westall (1981)	85.1
Grothwahl (1990)	75.8
Baker et al. (1997)	89.1

The observed organoclay K_{oc} values were between 3 to 6 times greater than those calculated; however, this is generally consistent with reported sorption of neutral aromatic compounds on organoclays (Nzengung et al., 1996; Lee et al., 1989; Boyd et al., 1988).

Combined Isotherm Parameters

Values as determined above for the constants K_{oc} , S_{max} , and k_L —for subsequent use in the combined isotherm—are summarized in Table 4.2 for the Na-clay and the three organoclays. The table also lists the sorbent cation exchange capacities and organic carbon contents.

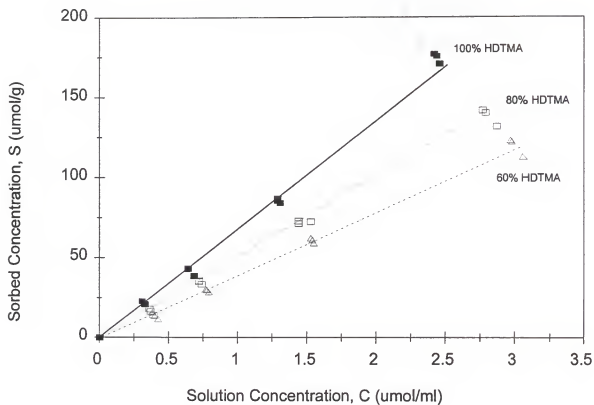


Figure 4.3. Sorption of quinoline on three organoclays at pH 8.

Table 4.2 Experimentally-determined constants for the combined isotherm.

Sorbent	CEC ($\mu\text{mol/g}$)	O.C. (%)	S_{max} (pH 3) ($\mu\text{mol/g}$)	$S_{\text{max}}/\text{CEC}$	k_L	K_{oc} (pH 8) (ml/g)
Na-clay	819	0.10	759	0.92	15.8	n/a
60% HDTMA	340	10.6	324	0.95	8.06	406
80% HDTMA	189	13.9	157	0.82	3.24	382
100% HDTMA	n/a	17.4	n/a	n/a	n/a	390

Exchange capacities and organic carbon contents for the partially-exchanged clays were consistent with the amounts of HDTMA added to the clay suspensions based on the CEC of the original Na-montmorillonite. The CEC of the 60% HDTMA clay was 41% of that for the original Na-montmorillonite, while that of the 80% HDTMA clay was 23% of the original CEC. The quinoline sorption maxima similarly reflected these proportions but, in this case, relative to S_{max} for the Na-clay.

It is notable that organoclay organic carbon contents were between 10.6 and 17.4%, which is quite high relative to most natural sorbents. However, this assessment must be balanced by recognition of the accompanying exchange capacities, which were also unusually high. Thus, it is the *relative* magnitudes of the organic carbon content and the cation exchange capacity, rather than the absolute abundance of either, that is central to the sorption of ionizable organic compounds.

Sorption maxima were somewhat lower than the observed exchange capacities, but this disparity is not a fundamental concern relative to application of the model. Sorbate-dependent variability of CEC determinations is well documented, and the sorption maximum for quinoline on the Na-clay *does* fall within the lower ranges of CEC established for this montmorillonite (Celis et al., 2000; Jaynes and Boyd, 1991; Westall et al., 1990). However, if lower values for S_{max} relative to the determined CEC are in fact a

consequence of the adsorption process for quinoline, characteristically low values could arise from a number of sources. Some of these will be discussed below.

Quinolinium adsorption has been shown to be vulnerable to competition from other cations (Ainsworth et al., 1987; Zachara et al., 1986), particularly at relatively low concentrations of quinoline in solution. Amelioration of competitive effects would be expected at higher quinolinium concentrations, but quinolinium concentrations remained well below those of the background electrolyte (Fig. 4.1). Thus, Na^+ competition may have been a minor mediating factor in determining the sorption maxima. At pH 3, H^+ or Al^{3+} also may have been competitors.

Ordinary steric factors likely did not play a role in the discrepancy between the CEC and S_{max} . Steric constraints on sorption of organic cations are based generally on their planar surface area in relation to the charge density and expansibility of the clay, since they prefer to adopt orientations that maximize contact between diffuse charge on aromatic rings and the clay surface. The largest reported planar surface area estimate for quinoline is 14.1 \AA^2 (Zachara et al., 1990; Helmy et al., 1983; Pearlman, 1980), and the van der Waals thickness of the quinoline ring is 0.67 nm. Organic cations with a planar surface area of about 50 \AA^2 are generally spatially compatible with smectite clays subject to their orientation at the mineral surface (Raussell-Colum and Serratos, 1987; Serratos, 1984).

The orientation of organic cations at the mineral surface, however, can be an important determinant of their sorption. Smectite clays diffuse charge over large areas, promoting strong electrostatic interaction with dispersed charge on the aromatic rings of NHCs. Formal charge calculations made by Zachara et al. (1990) showed that quinolinium's positive charge is distributed primarily among peripheral H atoms. As

indicated, adsorbed NHCs, including quinoline, prefer a planar orientation on montmorillonite surfaces (Zachara et al., 1990; Helmy et al., 1983; Hayes et al., 1978). There is evidence, however, to suggest an upright configuration for quinoline at high surface loadings (Helmy et al., 1983). Shift to an upright position requires the expenditure of greater energy for adsorption, while reducing the interaction of the cation aromatic rings with dispersed negative charge on opposing interlayer surfaces (Maes et al., 1980). This would tend to inhibit sorption as concentrations of surface species approached the CEC.

Alternatively, adsorbed HDTMA may have played a role in suppressing quinolinium exchange through reduced clay expansibility or restriction of quinoline access to the interlayer, particularly as surface loadings of HDTMA increased. X-ray analysis of these organoclays (Chapter 3) indicated that HDTMA and sodium ions could mutually occupy the same interlayers, particularly for the 60% organoclay and thereby observably influence expansibility of the mixed interlayers. It was also evident, based on sorption of naphthalene, that the distribution of Na^+ and HDTMA within the interlayer was neither uniform nor homogeneous, since for naphthalene sorption likely would require discrete organic domains for partitioning. This property could constrain interlayer access of quinolinium cations to particular "avenues" dictated by the proximity and arrangement of Na^+ and HDTMA, and impose diffusive constraints on exchange. This may have impacted the observed value of S_{max} with increased clay coverage by HDTMA.

Hayes et al. (1978) also reported adsorption maxima for mono-pyridinium cations that were 10-20% less than the CEC of montmorillonite clays. They believed that exchange at high surface loadings were constrained by interlamellar collapse during the early stages of adsorption. Incoming cations, subsequent to interlamellar collapse, would

be required to expend additional energy to penetrate the clay interlayers, resulting in adsorption maxima below the CEC. As a result they suggested that, as the exchange capacity was approached, selectivity for the adsorbing ions over resident surface cations should decline. This type of collapse is unlikely in the presence of HDTMA, but the selectivity for quinoline on montmorillonite has been shown to vary with surface coverage (Ainsworth et al., 1987).

Sorption at Intermediate pH on Two Fractionally-Exchanged Organoclays

Apart from their direct bearing on quinoline sorption in general, the above experiments at pH 3 and pH 8 were performed primarily as the basis for evaluation of the combined isotherm at other levels of pH for the 60% and 80% organoclays. In essence, they set the values for the parameters S_{\max} , k_L , and K_{oc} in the isotherm, which then could be applied directly to subsequent sorption data. These parameters were considered constant for each sorbent, with further model functionality dictated only by compound speciation. Favorable comparisons with the widely accepted Freundlich isotherm suggested that the combined isotherm may provide important additional information relative to sorption of the respective quinoline species.

The Freundlich isotherm

Initial assessment of quinoline sorption employed the Freundlich isotherm to provide an established frame of reference for subsequent evaluation of the combined isotherm. The Freundlich equation is empirical and, although coefficients derived from the linear form of the equation have been related to compound ionization and sorbent CEC in substrates of low organic carbon content, the relationships were the result of a systematic search for such correlations (Zachara et al., 1986). Nonetheless, subsequent evaluation of the data relative to the Freundlich isotherm (to be discussed in a later

section) further revealed the utility of the more mechanistically informative approach provided by the combined isotherm.

Freundlich fits to quinoline isotherms for pH values between pH 4 and 7 on the two fractionally exchanged organoclays are shown in Figs. 4.4 and 4.5. Table 4.3 lists Freundlich coefficients derived from the log-transformed data, as well as the equilibrium pH from each batch experiment. Freundlich isotherms routinely are reported for sorption of organic bases (Zachara et al., 1990; Ainsworth et al., 1987) and the Freundlich relation

Table 4.3. Freundlich isotherm coefficients for quinoline sorption on organoclays.

Sorbent	pH	K_f	N	r^2	K_{oc} (ml/g)
60% HDTMA montmorillonite	4.1	230	0.52	0.96	2169
	5.2	223.7	0.48	0.9	2110
	5.9	179.8	0.73	0.9	1696
	7.3	44.3	1.05	0.99	417
80% HDTMA montmorillonite	3.9	125.6	0.30	0.97	903
	5	127.1	0.44	0.99	914
	6.2	122.9	0.99	0.99	889
	7.2	58.7	1.00	0.99	422

performed quite well in describing the data. Linear correlation coefficients for the log-transformed data were typically high and in keeping with customary observations, but correlation between the Freundlich parameters K_f and N, and major sorbent or sorbate characteristics was generally absent—except for an observed variation of N with pH. This suggests an increasingly linear character to the isotherms as pH is increased. Moreover, normalization of the Freundlich coefficient, K_f , to the organic carbon content to yield an organic carbon partitioning coefficient, K_{oc} , obviously was not consistent. Instead, normalization indicated a substantial influence from cation exchange at lower pH values.

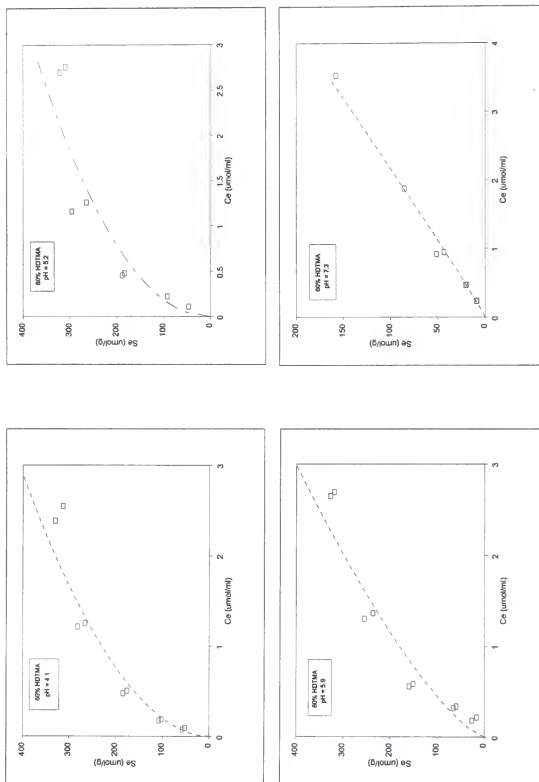


Figure 4.4. Freundlich isotherms for quinoline sorption on 60% HDTMA clay at four pH values.

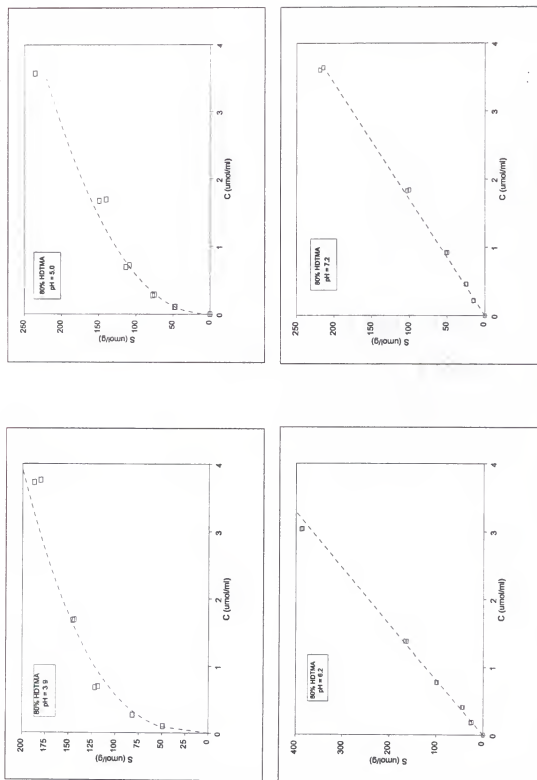


Fig. 4.5. Freundlich isotherms for quinoline sorption on 80% HDTMA clay at four pH values.

Normalization, however, did yield similar values for K_{oc} for both organoclays at high pH levels, where sorption is assumed to be dominated by organic partitioning of the neutral species.

The effect of exchange on the magnitude of K_f also was explored by comparing the K_f values for both organoclays. Table 4.4 compares the ratios of the sorption K_f with the ratios of CEC for the organoclays at four pH levels. It is apparent that K_f values were determined largely by exchange at lower pH values, as expressed by the exchange parameter, CEC.

Table 4.4. The influence of cation exchange on K_f .

pH	K_f 60%	CEC 60%
	K_f 80%	CEC 80%
4	1.83	1.79
5	1.76	
6	1.46	
7	0.75	

The combined isotherm

In contrast to the Freundlich isotherm, initial evaluation of the combined isotherm did not rely on any optimization of model parameters. Instead, the coefficients S_{max} , k_L , and K_{oc} as determined (i.e., calibrated) at pH 3 and 8 (Table 4.2) were enlisted directly to describe the data. Additionally, the individual contributions of the neutral and protonated species of quinoline to overall sorption were determined from the two terms in the combined isotherm. The magnitude of each term was determined solely by the concentration of either the neutral or protonated species, since all other model parameters were held constant for each sorbent. An example of the outcome is shown in Fig. 4.6 for quinoline sorption on the 80% HDTMA-organoclay at pH 5. Parameters in the model were

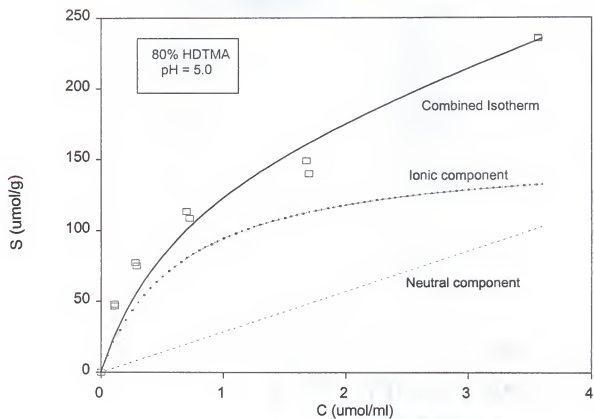


Figure 4.6. Illustration of the combined processes determining quinoline sorption.

obtained from Table 4.2 ($S_{\max}=156.88$ $\mu\text{mol/g}$, $k_L=3.06$, $K_{oc}=392.4$). This combination of pH, organic carbon content, and CEC was particularly illustrative of the modeled processes, insofar as the relative impacts of the neutral and ionized species were clearly delineated, and their combined effects on overall sorption apparent. Here, C_e is the equilibrium solution concentration of both species; S_e is the amount sorbed. The figure primarily illustrates the importance of both processes in determining the magnitude and shape of the isotherm. The ionized species dominated sorption at relatively low solution concentrations of quinoline, but the neutral species component accounted for almost half the total sorption at higher solution concentrations.

Quinoline Sorption on the 60% HDTMA-clay

The data in Fig. 4.7 shows sorption of quinoline through a progression in compound ionization between pH 4.1 and pH 7.3 on the 60% HDTMA-exchanged montmorillonite, demonstrating the relative contributions of the neutral and protonated species to overall sorption based on the two terms of the combined isotherm. The contribution of the neutral species at pH 4 was minimal, with the isotherm here naturally depending primarily on the ionic component. Conversely, the ionized species still contributed substantially to the complete isotherm even at pH 7.3, which is more than two units greater than the solute's pKa value. This is largely residual expression of the strong affinity for the cation relative to the neutral molecule.

Most interesting are the isotherms at pH 5.2 and 5.9, which encompass high concentrations of both species in a context that allows both to contribute substantially to overall sorption. At pH 5.2 both species exist in nearly equal proportions, while at pH 5.9 the neutral species—although a weaker contributor generally—nonetheless dominates in solution and can substantially impact sorption.

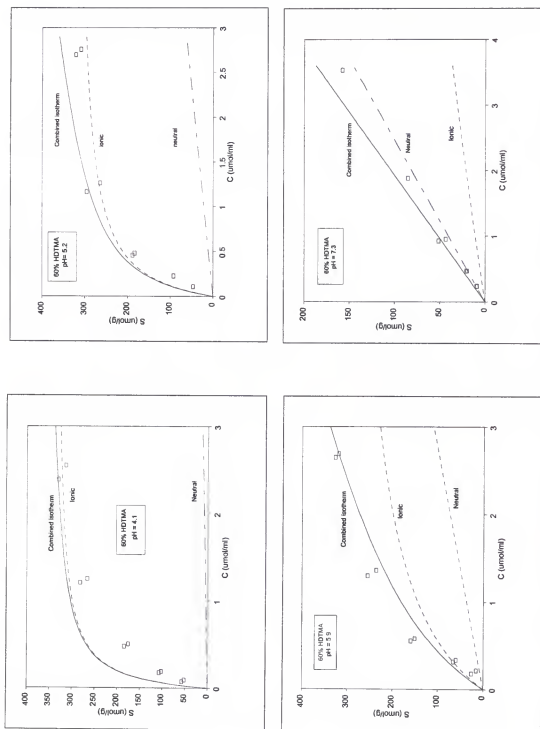


Fig. 4.7. Combined isotherm simulations from parameters determined at pH 3 and pH 8 on the 60% organoclay at four pH values.

Total sorption at pH 5.2 attained levels in excess of the CEC, confirming the influence of mechanisms other than cation exchange. Addition of the neutral species contribution to the ionic contribution afforded a more accurate description of the data at high concentrations in solution, although the isotherm was not materially affected at concentrations less than about 0.25 $\mu\text{mol/mL}$. The data were also over-predicted at lower solution concentrations, which may have been a result of the mixed HDTMA-Na interlayers observed for the 60% organoclay (Chapter 3). Mixed interlayers mandate simultaneous accommodation of both the neutral and ionic species of quinoline in the interlayer at intermediate levels of pH. Single-species sorption at pH 3 and pH 8, which determined the isotherm coefficients S_{max} , k_L , and K_{oc} , was not subject to this constraint and, therefore, may not have reflected interactions between species which could have reduced sorption at other pH values.

Although the neutral species is frequently discounted as a major contributor to overall sorption, the neutral form had a substantial impact on sorption at pH levels near or in excess of the solute's pKa value. The combination of high organic carbon content relative to the CEC and the abundance of the neutral species in solution rendered the overall process highly dependent upon the organic partitioning term of the isotherm. The pH 5.9 isotherm concisely illustrates this point, with approximately 1/3 of the total sorption at solution concentrations above 2.5 $\mu\text{mol/mL}$ being ascribed to the neutral species. Thus, addition of the neutral component to ionic sorption above the solute pKa was critical to accurate description of the data. Further, the neutral species ultimately dominated sorption at pH 7.3, although the ionic component still remained important. Strong affinity of the ionized species for clay surfaces apparently somewhat overcame the

relative scarcity of the cation in solution, a circumstance that has been described previously.

Quinoline Sorption on the 80% organoclay

The 80% organoclay possessed a lower proportion of cation exchange capacity in relation to the organic carbon content, which magnified the role of the neutral species in sorption. This resulted in a dominance of the partitioning term at generally lower pH values than for the 60% organoclay. Nonetheless, overall results were analogous to those for the 60% clay. A progression in compound ionization is again shown in Fig. 4.8. In this case, the combined isotherm generally tended to underestimate sorption (particularly at pH 6.2), which may suggest contributions from mechanisms other than those modeled. It was noted that, when k_L was optimized in the combined isotherm (to be presented below), the determined values tended to exceed those determined from the pH 3 isotherm on the 80% HDTMA-clay. As a fitted parameter in this context, k_L potentially could encompass sorptive contributions from sources not considered by the model—for example, the interaction of hydrophobic substituents on quinolinium with adsorbed HDTMA.

Naturally, the combined isotherm also indicated that the neutral species assumed a greater role in sorption on the 80% organoclay compared to the 60% organoclay that was commensurate with the increase in the fraction of organic carbon. The sorbate parameter K_{oc} was held constant, but the fraction of organic carbon, f_{oc} , was greater in the linear term. The parameters S_{max} and k_L also were lower in the exchange term than for the 60% organoclay. Thus, the isotherm suggested that the neutral species dominated sorption above pH 6, and was almost completely responsible for sorption at pH 7.2.

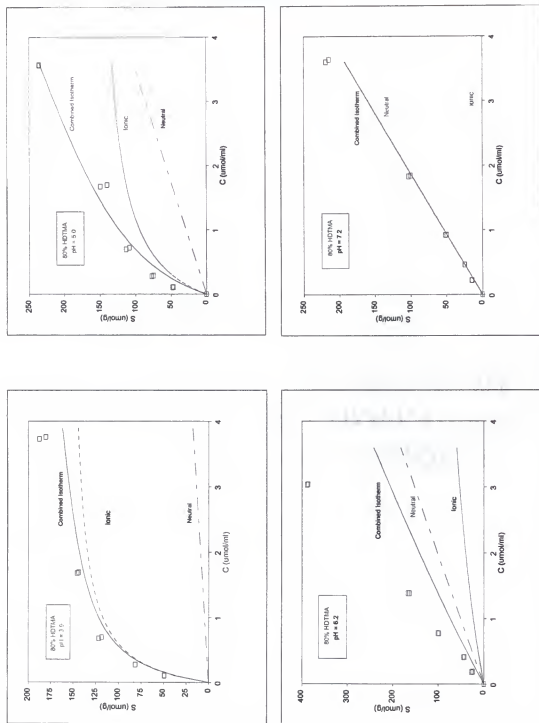


Figure 4.8. Combined isotherm simulations for parameters determined at pH 3 and pH 8 on the 80% organoclay.

Comparison with the Freundlich Isotherm

For both of the partially exchanged organoclays, it was evident that the combined isotherm described the shape and magnitude of the data fairly well, despite employing independently determined isotherm coefficients. The major exception was for the 80% organoclay at pH 6.2. The implication is that sorption on organoclays can be approximated given reasonable estimates of S_{\max} , k_L , and K_{oc} . Thus, the combined isotherm applied to a highly controlled sorbent system offered a mechanistically referenced approach to quinoline sorption that is absent in the broadly applied Freundlich model. Further, at least two of the model coefficients, S_{\max} and K_{oc} , bear a practical relation to widely catalogued or easily determined sorbent and sorbate properties. The Freundlich isotherm must be directly fit to a given data set to obtain the appropriate coefficients, and relating these to either sorbent or sorbate properties historically has been a matter of correlation without the benefit of a direct theoretical basis.

As discussed, Freundlich equation fits to the present data were quite good (Table 4.3). Freundlich isotherms derived from regression of the linearized data are compared to the combined isotherm model for the 60% and 80% HDTMA clays in Figs. 4.9 and 4.10, respectively. In general, the Freundlich isotherm was superior for describing the data, but it should be recalled that the combined isotherm, unlike the Freundlich relationship, was not directly fit to the data, and none of the model parameters was optimized.

Optimization of k_L

A logical step to reconcile these two approaches was to compare them on a more equivalent basis by direct fitting of the combined isotherm as well. Direct-fitting potentially could involve optimization of three parameters: S_{\max} , k_L , and K_{oc} . However, S_{\max} and K_{oc} were based on sorbent or sorbate properties that are difficult to ignore in

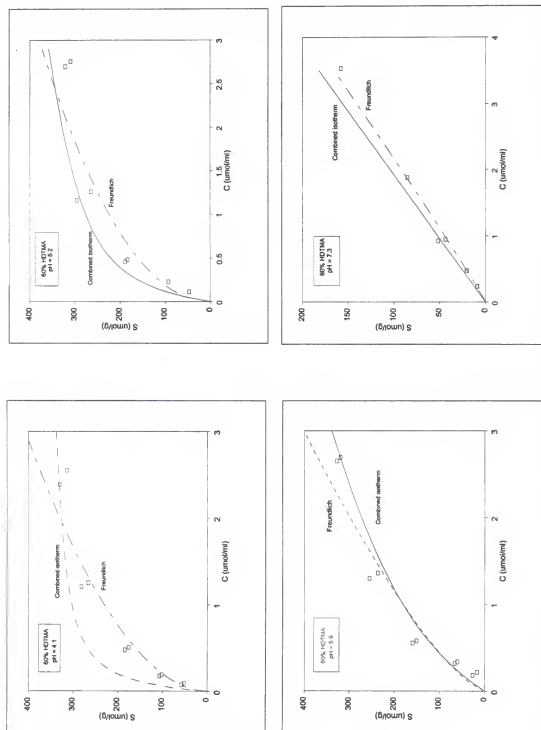


Figure 4.9. Comparison of combined isotherms and Freundlich isotherms for quinoline on 60% HDTMA clay at four pH values.

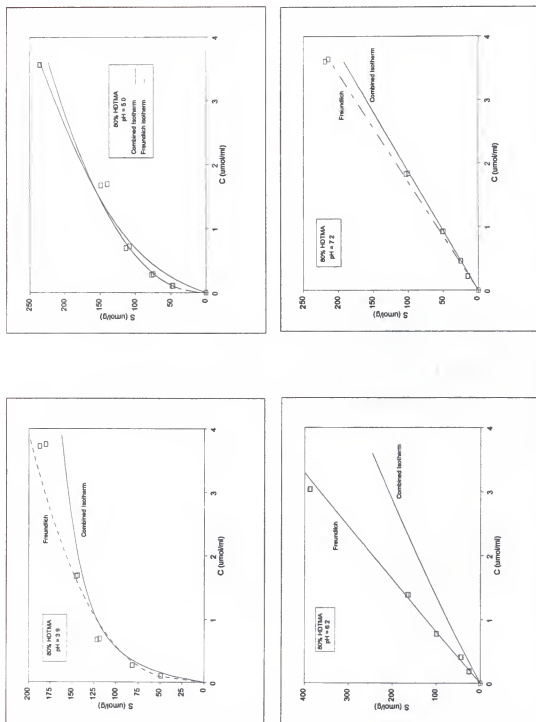


Figure 4.10. Comparison of combined isotherm and Freundlich isotherms for quinoline on the 80% HDTMA clay at four pH values.

favor of a multi-parameter optimization. The parameter k_L was the most tenuous in terms of its relation to definable properties.

In the derivation of the Langmuir term of the combined isotherm, k_L was related to the exchange coefficient K_{ie} (Chapter 2), through the expression $k_L = K_{ie}/(Na^+)$. Empirically, k_L sets the slope of the Langmuir equation at low solute concentrations, and is frequently regarded as an “affinity coefficient” that traditionally has been deemed proportional to the energy of adsorption (Sposito, 1979; Cavallaro and McBride, 1978; Harter and Baker, 1977). It is sometimes believed, therefore, that the relative affinity of two solutes for a given sorbent can be expressed through k_L , but several authors warn against liberal interpretations of the parameter (Sposito, 1979; Griffin and Au, 1977; Harter and Baker, 1977). Predicting k_L in a meaningful way also is not straightforward. Comparing even true affinity parameters for exchange from different experiments on different sorbents is not necessarily warranted unless the equilibrium solutions are identical for each point on the isotherm, because the parameter is also proportional to the competing ion concentration (Sposito, 1979).

As stated, the values for k_L in the Langmuir term of the combined isotherm determined at pH 3 declined systematically with increased HDTMA coverage, implying a consonant reduction in selectivity. However, the application of k_L as an affinity parameter is probably unwarranted for this type of sorbent. Values and predictors of k_L also are neither widely agreed upon nor documented, which strengthens its candidacy for optimization.

Figs. 4.11 and 4.12 compare the optimized combined isotherm and Freundlich isotherms across the range of pH for the 60% and 80 % organoclays, respectively. The optimized k_L values are presented in Table 4.4

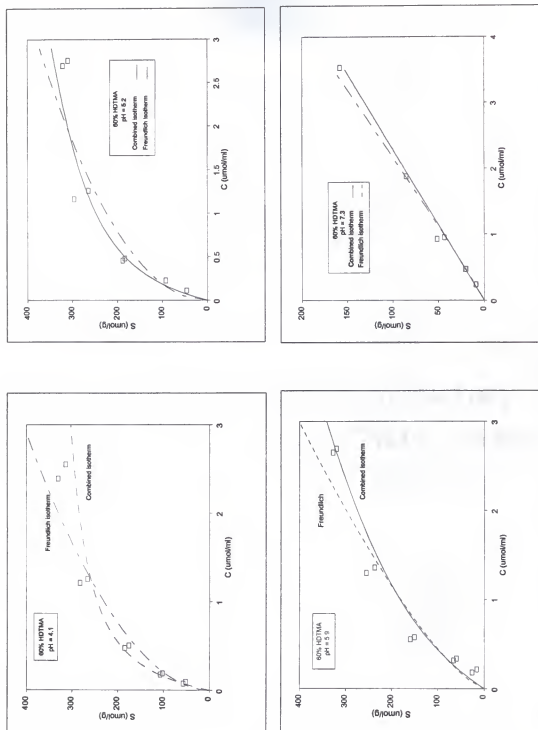


Figure 4.11. Comparison of optimized combined isotherms and Freundlich isotherms for quinoline on the 60% HDTMA clay at four pH values.

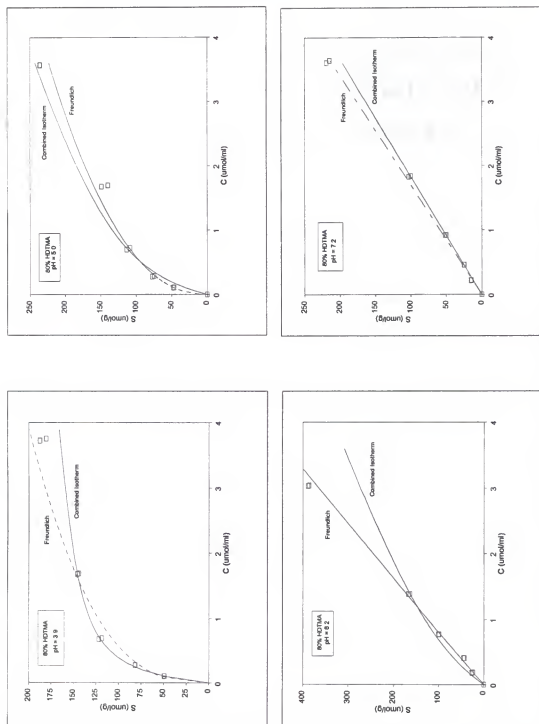


Figure 4.12. Comparison of optimized combined and Freundlich isotherms for quinine on the 80 % HDTMA clay at four pH values.

Table 4.4. Optimized values of k_L

Sorbent	pH	k_L	r^2
60% organoclay	4.1	3.20	0.99
	5.2	4.71	0.95
	5.9	8.06	0.95
	7.3	1.54	0.96
80% organoclay	3.9	4.71	0.97
	5.0	4.32	0.97
	6.2	18.89	0.90
	7.2	10.17	0.99

Two factors seem evident. Given reasonable values for S_{\max} , K_{oc} , and f_{oc} determined from relevant sorbate or sorbent properties, optimization of k_L results in a quite-accurate description of the experimental data. Additionally, and perhaps more germane, the comparison demonstrates that the combined isotherm can assume a form that closely mimics the Freundlich isotherm while remaining mechanistically informative.

Optimized k_L Values

Optimized values of k_L varied non-systematically with pH, attaining a maximum value near pH 6 for both fractionally exchanged clays (Fig. 4.13). As a fitted parameter in this context, k_L encompasses the combined impact of both quinoline species rather than necessarily indicating an increase in affinity for the cation alone, since overall sorption also was generally highest at this pH. Therefore, because the partitioning term of the combined isotherm is probably a more reliable measure of the aqueous-organic component of sorption, the optimized k_L likely encompasses the totality of other mechanisms, insofar as they contribute to the Langmuir term, apart from and including

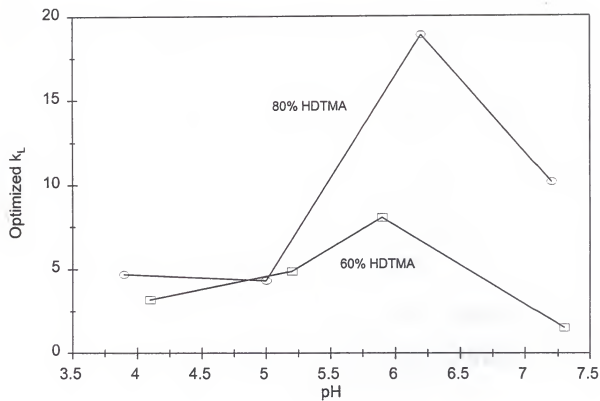


Figure 4.13. Optimized k_L values as a function of pH.

cation exchange. In other words, it is an empirical coefficient, and although the use of organoclays was designed to limit the impact of “extraneous” mechanisms, consigning them to the fitted parameter was effective in terms of model application.

Evidence of increased sorption near pH 6 has been reported previously for high concentrations of quinoline on pure clays (Helmy et al., 1983). Such behavior has been explained in terms of decreased competition from H^+ as pH increased, combined with a belief that the neutral molecule is especially well accommodated at montmorillonite surfaces. This could lead to greater sorption as the pH approached 6, where Helmy et al. (1983) estimated that two-thirds of the adsorbed molecules were neutral. Sorption of quinoline likely was facilitated by hydrophobic interactions between incoming cations and those previously sorbed, particularly in view of the high concentrations employed, up to 17 $\mu\text{mol/ml}$ in solution (Traina and Onken, 1991; Maugulies et al., 1988; Ainsworth et al., 1987).

Single-point isotherms like those employed by Helmy et al. (1983), however, where sorption from a single initial solution concentration is compared across a range in pH, are susceptible to misinterpretation. For example, Nichols and Evans (1991) postulated that surface protonation reactions for organic bases (Voudrias and Reinhard, 1986; Karickhoff and Bailey, 1976; Mortland, 1970) facilitated cation adsorption above the solute's pKa value. This was based on the observation that the sorption coefficient, k_d ($k_d=S/C$), was one half its maximum value at a pH more than one unit greater than (not equal to) the pKa of 4-methoxyaniline. At $\text{pH}=\text{pKa}$, the compound is 50% ionized, hence, the assumption that sorption should equal one-half of its maximum level based on cation exchange considerations alone. This approach, however, assumes that the shape of the

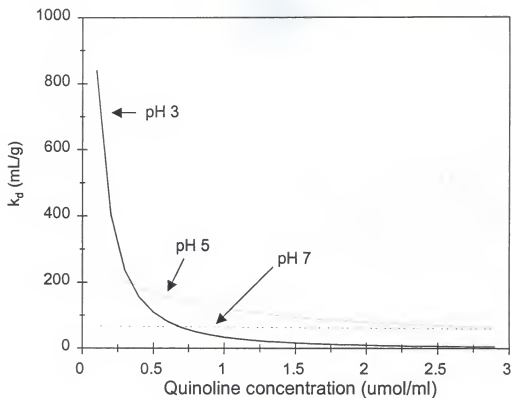
single-point isotherm is independent of the equilibrium concentration. In other words, it assumes that the isotherms at individual levels of pH are linear.

To the contrary, the magnitude of k_d is dependent on both the equilibrium solution concentration and pH, and must be calculated for each point on the individual isotherms for valid comparison. Equation 4.2 indicates the sorption coefficient determined from the derivative of the combined isotherm (Appendix A)

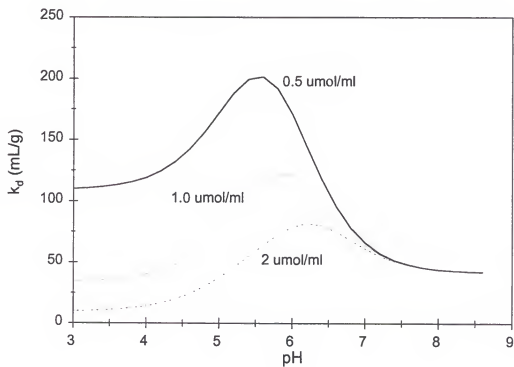
$$k_d = \frac{S_{\max} k_L \epsilon}{(\epsilon + k_L C_T)^2} + K_{oc} f_{oc} \frac{(\epsilon - 1)}{\epsilon} \quad (4.3)$$

where C_T is the total equilibrium quinoline concentration and ϵ equal $1 + 10^{(pH - pK_a)}$, and describes speciation of the compound in solution. Therefore, the magnitude of k_d depends on concentration pH and pKa. Data in Fig. 4.14a illustrate k_d as a function of solution concentration at several pH values on the 60% organoclay for a chemical with a pKa value of 5.0. The parameters S_{\max} , k_L , f_{oc} , pH, and K_{oc} were held constant for each curve. As expected, the sorption coefficient was greatest at low concentrations, due to the slope of the ionic term of the combined isotherm. Moreover, increased pH results in a “flattening” of the curve due to the increasing dominance of the neutral term, which has a constant slope.

Fig 4.14b indicates the effect of pH on k_d when concentration is held constant at three different levels. Interestingly, the maximum value of k_d is in the vicinity of the compound pKa. Its actual position, however, is dictated by both concentration as well as the magnitude of the other parameters (e.g. S_{\max}). One implication is that maximum solute retardation during transport will be at intermediate pH values rather than at either extreme. Additionally, it is apparently difficult to reach concrete conclusions based on



(a)



(b)

Figure 4.14. Sorption coefficient k_d as a function of (a) concentration and (b) pH.

macroscopic observations of single point isotherms unless they are evaluated at a single equilibrium concentration.

Contributions of the Neutral and Protonated Species to Sorption

Data in Figs. 4.15 and 4.16 show contributions of the two NHC species to overall sorption based on the optimized combined isotherm. As expected, the neutral species had little impact on sorption below the pKa value for quinoline. Above the pKa, however, the neutral species component was critical to accurate description of the data. This was especially true near and above pH 6, where sorption was strongly influenced even at relatively low concentrations of the base in solution. Influence of the neutral species also naturally was linked to the amount of organic carbon relative to the CEC. The ratio of organic carbon to CEC for the 80% organoclay was more than twice that for the 60% clay. Thus, determinations for the 80% organoclay indicated a dominance of the linear term of the isotherm at generally lower pH values. As discussed, organoclay partitioning domains are particularly effective in the uptake of the neutral species from solutions. The ability of natural organic matter in soils to similarly impact sorption will be addressed in Chapter 5.

Conclusions

Separation of the actions of the neutral and ionized species within their relevant sorbent volumes provided a compelling basis for a multi-mechanistic approach to overall organic base sorption. Factoring all or even most of the sorptive contributions for a more complex sorbent may be more difficult, but simple separation of the dominant processes in clays and organoclays lent credence to the view that organic base sorption, although frequently related to exchange parameters on the sorbent, embraces processes beyond cation exchange.

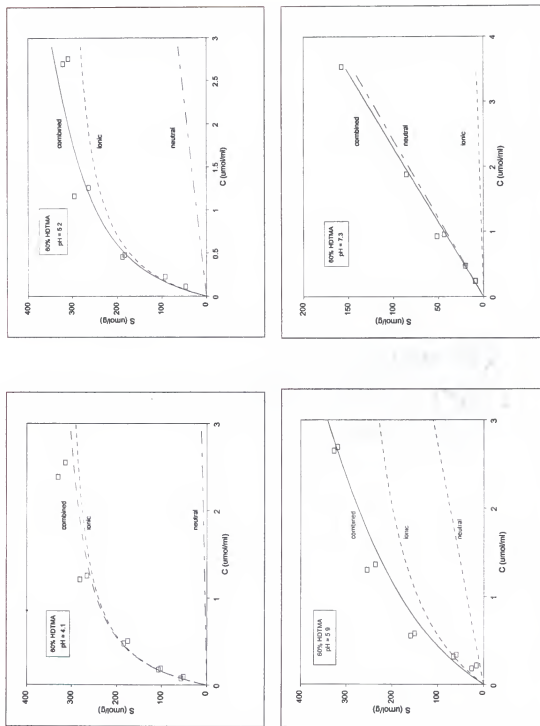


Figure 4.15. Neutral and protonated species sorption for the 60% organoclay from the optimized combined isotherm at four pH values.

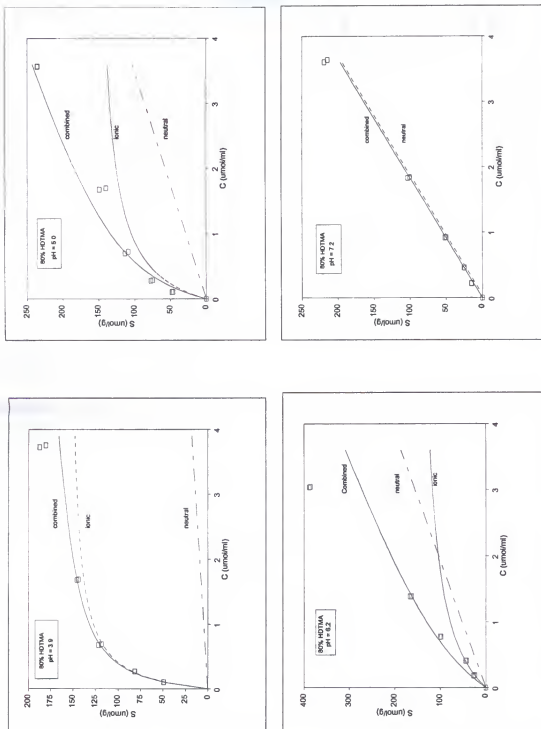


Figure 4.16. Neutral and protonated species sorption for the 80% organoclay from the optimized combined isotherm at four pH values.

Langmuir isotherms were obtained for low pH values and, despite an overt as well as a subtextual debate in the late 1970s concerning the applicability of this isotherm for cation exchange (Harter, 1979; Shukla and Mittal, 1979; Sposito, 1979; Harter and Baker, 1977), it performed well as an empirical component in the combined isotherm.

The neutral-species component of the model obviously was exaggerated through the use of organoclays which, in addition to their high organic carbon contents, also exhibit a particularly marked affinity for neutral organics. It should be noted, however, that the magnitude of the cation exchange capacity in relation to the organic carbon content of the partially-exchanged organoclays fell within the range of many soils. Nonetheless, the objective in the present context was not necessarily to promote an extrapolation of these results to other more complex media (nor to rule it out), but instead to demonstrate the utility of a mechanistically-sensible approach that accords with the majority of the existing experimental data. Also, while it is acknowledged that the exchange/adsorption component is a powerful determinant of sorption, the combined isotherm provides insight to, and an observable measure of, the magnitude of the neutral species contribution however small or large.

Additional testing is warranted, particularly to address the impact of the neutral species component of the isotherm and the relevance of the combined isotherm for more complex sorbents. Quinoline is a moderately hydrophobic organic base and this, in conjunction with the affinity of HDTMA clays for neutral species, may have disproportionately emphasized the organic partitioning term of the model. Therefore, Chapter 5 will examine the combined isotherm approach to describe NHC sorption on soils.

CHAPTER 5 SORPTION OF N-HETEROCYCLES ON SOILS

Introduction

Quinoline sorption on partially exchanged organosmectites (Chapter 4) illustrated both the utility of the combined isotherm and the apparent soundness of its theoretical foundation under closely controlled conditions relative to the composition of the exchanger and organic phases. Sorbent exchange capacity resided entirely within a well-defined mineral fraction; none arose from characteristic functional groups (COOH, OH) on organic matter. Further, the organic phase was non-polar and essentially uniform over the pH range in question with respect to its effect on sorption of the neutral species. The organic phase, although variable in physical configuration, also apparently could be independently defined in terms of its impact on sorption of the neutral species.

A natural subsequence of this work might involve the extension of the principles learned to natural sorbents in which these conditions could not be actively controlled. Five soils were investigated, representing a pH range between 3.6 and 7.2. Organic carbon contents were between 0.36 % and 3.84 %, and exchange capacities varied from 6.2 mmol/kg up to 250 mmol/kg. Unlike many previous studies (Banwart et al., 1982; Zachara et al., 1986), the goal was not the elucidation of a single element of sorption or the search for correlative indicators under narrowly defined conditions. Instead, the aim was to allow the varied elements of overall sorption to freely operate, and then to use the combined isotherm to delineate the two dominant mechanisms believed to be responsible.

It was evident that, rather than the absolute magnitude of the various sorption parameters defined by the combined Langmuir-linear isotherm or the abundance of any single soil component, the most critical elements were their joint combinations or their concerted impacts on the sorption process.

Quinoline initially was used as a representative probe compound, but additional work using two other NHCs (both a higher and a lower molecular weight compound) further illustrated applicability of the combined isotherm and its utility in a more mechanistically informative approach than has traditionally been employed.

Background

Conventional sorption studies on soils of nitrogen heterocyclic compounds like quinoline differ from one another in two chief respects: the nature of the adsorbates, and the soil or sediment's organic carbon content. Studies by Banwart et al. (1982) and Zachara et al. (1986) are representative examples. Banwart et al. (1982) examined sorption of three high molecular weight N-heterocycles—biquinoline, acridine and dibenzocarbazole—on sediments, and determined that sorption was driven by solvophobic partitioning into the sediment organic fraction. Organic carbon contents ranged from 0.11 to 2.38% and sediment pH varied between 4.5 and 8.5. The isotherms for these compounds were linear, and generally conformed to traditional K_{oc} - K_{ow} and K_{oc} -solubility relationships derived for a number of polynuclear aromatic hydrocarbons (Karickhoff et al., 1979).

Alternatively, Zachara et al. (1986) related sorption (specifically, the Freundlich sorption coefficient, K_f) to the ionized species in solution and the cation exchange

capacity. In effect, the exchange-normalized Freundlich sorption coefficient, K_d/CEC (Chapter 1), was strongly correlated with the predominance of the exchangeable species in solution. However, the experiments were designed specifically to examine the role of organic cations in sorption; thus, they were conducted on soils of low organic carbon content, which would tend to obviate the impact of the neutral species on sorption and, therefore, on K_d . Of the nine soils used by Zachara et al. (1986), six had organic carbon contents less than or equal to 0.35%, and only one had an organic carbon content greater than 0.60%.

By comparison, eight of the sediments examined by Banwart et al. (1982) had organic carbon contents greater than the highest tested by Zachara et al. (1986). This combined with the much greater hydrophobicities of acridine, biquinoline, and dicarbendazole relative to quinoline—likely contributed to the disparate results. For example, the octanol-water partitioning coefficient for quinoline is approximately 42 times less than that of acridine, and 200 times less than that of biquinoline. The implication is that lower molecular weight, higher solubility compounds like quinoline would not be greatly subject to solvophobic forces in the aqueous phase. Thus, sorption would be almost entirely due to cation exchange.

It can be argued, however, that the magnitude of cation exchange and solvophobic partitioning are related for organic bases, because the same factors promote both mechanisms. Recall that, beyond the strictly electrostatic component to exchange of organic cations, is a *non-coulombic* component. In essence, the hydrophobic substituents on organic cations interact with mineral surfaces, appreciably augmenting exchange

strength. This interaction is regarded as largely responsible for the tenacity with which organic cations are adsorbed. Thus, the molecular substituents responsible for the partitioning of organic compounds into the organic fraction of soils and sediments also have a role in exchange.

Clearly, organic partitioning is linked to the size of the neutral substituent of a molecule. Likewise, adsorption via exchange has been shown to depend on the size of the cation or, more specifically, the size of the hydrophobic portion of the cation. The best illustration of this was provided by Cowan and White (1958) who studied the adsorption characteristics of *n*-alkylammonium cations with incrementally increasing numbers of carbon atoms in their alkyl chains (Fig. 5.1). The intercept of the ordinate in Fig. 5.1 represents the energy associated with the electrostatic component to exchange. This energy is characteristic of the root compound of the homologous series and depends on such factors as hydration, size of the non-hydrophobic portion of the ion, electronegativity, and charge. However, with each carbon addition to the molecule, the energy of adsorption—represented by the Gibbs free energy (ΔG_{ads})—increased in a roughly linear fashion. An analogous observation can be made concerning the partitioning of neutral solutes into organic carbon. Increases in the size of the hydrophobic portion of neutral molecules yield a commensurate increase in absorption.

Thus, the same factors that determine the strength of sorbate interaction with organic carbon also may impact cation exchange. As the size of the hydrophobic portion of the sorbate and, consequently, its interaction with organic carbon declines, so does the strength of exchange and the selectivity of the ion over other cations. Therefore, the rela-

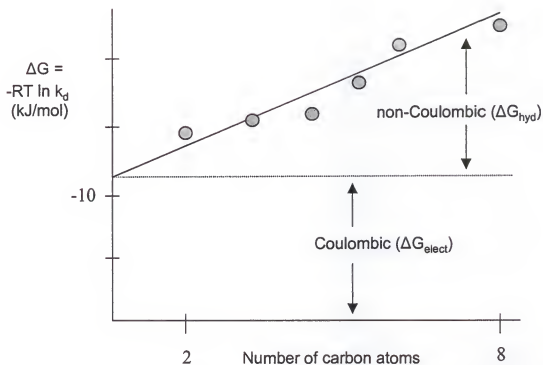


Fig 5.1. Relationship between the energy of adsorption and the number of carbon atoms in the alkyl substituent, where k_d is a sorption coefficient, ΔG is the Gibbs free energy, R is the ideal gas constant, and T is the temperature. Adapted from Cowan and White (1958)

tive influences of exchange and solvophobic partitioning on overall sorption as molecules become less hydrophobic may diverge less than anticipated. In other words, the two modes of sorption rise and fall together to some extent. From the standpoint of total sorption, only the electrostatic component of cation exchange remains comparatively constant, despite differences in the hydrophobic portions of the molecules.

Consider the analogues to acridine-quinoline and pyridine. With decreasing ring number the molecules become less hydrophobic. The octanol-water partition coefficients for the three compounds are 4200, 107, and 10, respectively (Table 5.1). Since exchange of the organic cation at low pH is driven in part by non-coulombic interaction of the neutral portion of the molecule with exposed clay surfaces, the cation selectivity, here represented by the conditional selectivity coefficient, ${}^c k_{ex}$, declines as well. The values of ${}^c k_{ex}$ are conditional with respect to solid phase activities, and were determined by Zachara et al. (1990) based on the exchange equation:



where NaX and QHX are sodium and the ionized organic base, respectively, on the exchange complex and Na^+ and BH^+ are the solution species. The exchange coefficients were calculated with respect to mole fractions of sodium and quinoline on the exchanger (X_{Na} and X_{QH} , respectively)

$${}^c k_{ex} = X_{BH} (Na^+)/X_{Na} (QH^+) \quad (5.2)$$

where Na^+ and BH^+ are solution species.

Table 5.1. Sorption-related properties of three N-heterocycles
(adapted from Zachara et al., 1990)

Compound	Rings	Log K_{ow}	Selectivity	Planar surface
			Log $^cK_{ex}$ ^{*1}	Area (nm ²)
Acridine	3	3.40	3.00	1.85
Quinoline	2	2.04	2.12	1.41
Pyridine	1	1.00	1.47	0.98

^{*1} calculated from sorption on specimen (Swy-1) and natural smectites.

In Fig.5.2 an illustration of the relationship between the exchange coefficient and the octanol-water partition coefficient relative to ring number on the organic molecule based on these calculations is shown. It shows that, while solvophobic partitioning into the organic phase—represented by K_{ow} —declines with decreasing ring number, there is a coincident decline in the exchange coefficient. This suggests that the *relative* magnitudes of the two mechanisms might be maintained.

Such a comparison between these coefficients is not simple, since k_{ex} must account for the counter ion on the exchanger and in solution. It does serve, however, to illustrate the potential interdependence between the coefficients. The decline in the octanol-water partitioning coefficient with decreasing ring number is accompanied by a reduction in the magnitude of the exchange coefficient that, although not necessarily equivalent, may indicate a more significant role for solvophobic partitioning in overall sorption (given sufficient organic carbon) that should be investigated.

Materials and Methods

Soils

Soils samples were obtained from a repository on the University of Florida campus, and were selected based upon pH, cation exchange capacity, and the organic

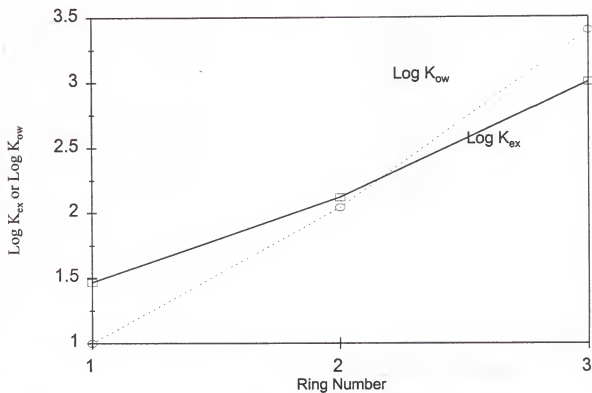


Figure 5.2. Comparison of the exchange coefficients and the octanol-water partitioning coefficients for pyridine, quinoline, and acridine.

carbon content reported. Actual values for these parameters were determined in the lab. The soils were initially collected as part of the State's soil survey efforts. The Felda soil is a loamy, siliceous, hyperthermic arenic aqualf. Lochloossa is a loamy siliceous, hyperthermic aquic paleudult. The Eustis soil is a sandy siliceous, thermic psammentic paleudult. The Webster is a fine-loamy, mixed, mesic typic endoquall. The Mandarin soil is a sandy, siliceous, thermic, oxyaquic alorthod. Initial pH was measured in 0.01 M CaCl_2 , with values reported for individual experiments being measured in the equilibrium solutions. Cation exchange capacity was determined by barium-magnesium ion exchange (Rhoades, 1982) at the original soil pH. Organic carbon content was determined using the Walkley-Black method. Soils received no pre-treatment prior to their use in the batch experiments. The goal was to determine sorption on soils in essentially their natural state, except for subsequent air-drying.

Chemicals

Reagent grade 2-methylpyridine, quinoline, and acridine were obtained from Aldrich Chemical Co., with the former two compounds being liquids and the latter a yellow solid. The acidic form of 2-methylpyridine, quinoline and acridine have pKa values of 6.00, 4.92, and 5.62, respectively (Zachara et al., 1990; Perrin et al., 1981). Therefore, they can exist as cations or neutral molecules at environmentally relevant pH values.

Sorption experiments

Equilibrium sorption of 2-methylpyridine, quinoline, and acridine from aqueous solution on all soils was examined using a stirred batch method (Nkedi-Kizza et al., 1985). It was desirable to control the ultimate equilibrium concentrations within similar

ranges for all three compounds. Therefore, the solution:soil ratios and initial concentration ranges varied somewhat depending on the compound used, its extent of sorption, and its solubility. For 2-methylpyridine and quinoline, solution:soil ratios were 8:1, but for acridine they were 75:1. This reflects the relative strength of sorption for acridine (as well as its solubility) compared to the other two compounds. Initial 2-methylpyridine solution concentrations were between 0.12 $\mu\text{mol/mL}$ and 1.20 $\mu\text{mol/mL}$. Quinoline solution concentrations were essentially twice those for 2-methylpyridine and acridine concentrations were between 0.025 $\mu\text{mol/mL}$ and 0.10 $\mu\text{mol/mL}$. The pH was adjusted through addition of either HCl or NaOH, soil was weighed into 30-ml polypropylene centrifuge tubes, and the appropriate solutions were added. The tubes then were shaken at ambient temperature (25°C) for 24 hours. Equilibrium solutions were obtained by centrifugation and subsequent sampling of the supernatant. Equilibrium chemical concentrations were determined by High Performance Liquid Chromatography (HPLC) using ultraviolet detection ($\lambda = 280$), a C-18 column, and a 0.10 M ammonium acetate:methanol mobile phase in a ratio of 70:30. Sorbed chemical concentrations were determined as the difference between the amounts added to each tube and that remaining in the equilibrium solution.

RESULTS AND DISCUSSION

Sorption of Quinoline: The Freundlich Isotherm and the Role of Cation Exchange

Similar to sorption on organoclays (Chapter 3), soil isotherms generally conformed to the Freundlich relationship and gave good fits to the linear form of the equation:

$$\text{Log} S = \text{Log } K_f + N \text{ Log } C_e \quad (5.3)$$

where S is the amount of sorbed organic base ($\mu\text{mol/g}$), C_e is the equilibrium solution concentration, and K_f and N are Freundlich sorption coefficients. These coefficients as well as the linear correlation coefficients for all soils are listed in Table 5.2.

Table 5.2. Freundlich isotherm parameters for quinoline on five soils.

Soil	pH	CEC ((mmol(-)/kg)	Organic Carbon (%)	K_f (ml/g)	N	r^2
Felda fine sand	3.6	11.02	0.36	9.58	0.54	0.98
Mandarin fine sand	4.9	8.02	1.42	4.49	0.59	0.99
Lochloosa sand	5.5	6.12	0.84	6.09	0.75	0.84
Eustis fine sand	6.1	12.04	0.64	1.16	0.87	0.97
Webster silt loam	7.2	250.4	3.84	27.33	1	0.96

The Freundlich relationship frequently is employed to model sorption data for organic bases and has been extended to include correlation between the Freundlich coefficient, K_f , and soil properties such as pH, CEC, and organic carbon content. However, there has been no consistent correlation observed between K_f and any *single* sorption variable, since sorption obviously depends on experimental conditions related to the pH range, the nature of the adsorbate, and the soil organic carbon content.

For example, the Freundlich coefficient, K_f for quinoline, when normalized to the CEC, has been related successfully to the concentration of the ionized species in solution as discussed above (Zachara et al., 1986). In effect, the exchange-referenced sorption coefficient (K_f/CEC) for a number of soils with low organic carbon content was correlated with the fraction of the exchangeable species in solution. Fig. 5.3 illustrates the relationship between K_f/CEC and the ionized fraction in solution we obtained for quinoline in 0.01 CaCl_2 solutions. The correlation ($r^2=0.87$) was weaker than that

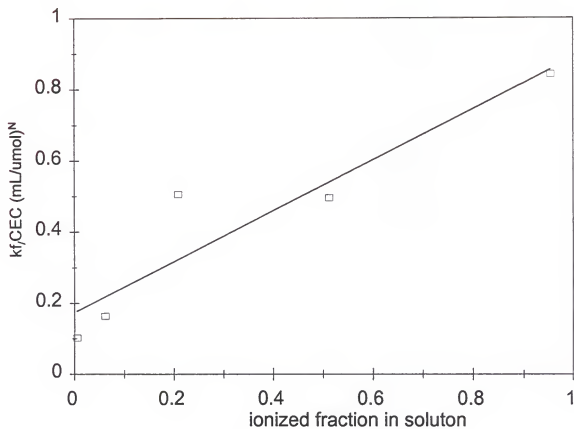


Figure 5.3. Correlation of the exchange-normalized Freundlich coefficient with the ionized species fraction in solution for quinoline on five soils.

observed by Zachara et al. (1986). However, for the present data, organic carbon contents were as high as 3.84% in the Webster soil. Therefore, the opportunity for interaction of the neutral species with organic carbon may have influenced K_f in a manner unrelated to exchange, and biased correlations between exchange-referenced sorption and the predominance of the ionized species in solution. The extent of such "bias", however, is impossible to deduce from the Freundlich isotherm.

Nevertheless, it is apparent that cation exchange is a powerful and perhaps dominant component of overall sorption. In Fig. 5.4, the relative effects of quinoline sorption from deionized water and 0.01 M CaCl_2 solutions are represented. The plot indicates an overall reduction in sorption at all levels of pH in CaCl_2 compared to deionized water solutions, implying competitive effects from Ca^{2+} . Also, the differences in sorption, with and without the background electrolyte, diminished with increasing pH. This implies that competition from Ca^{2+} also declined at higher pH which, in turn, suggests that the neutral species may have assumed an increasingly greater role in sorption. In terms of competitive effects, the data were most consistent with the postulate of Zachara et al. (1986).

The Combined Isotherm

Based on the above results, the Freundlich isotherm provided a rudimentary basis upon which to model sorption data for organic bases in this group of soils. However, it did not necessarily reveal the mechanisms implicated in sorption, nor did it offer a direct means to assess the relative impacts of these mechanisms. Alternatively, the combined isotherm assumes additive contributions to sorption from both adsorption and organic

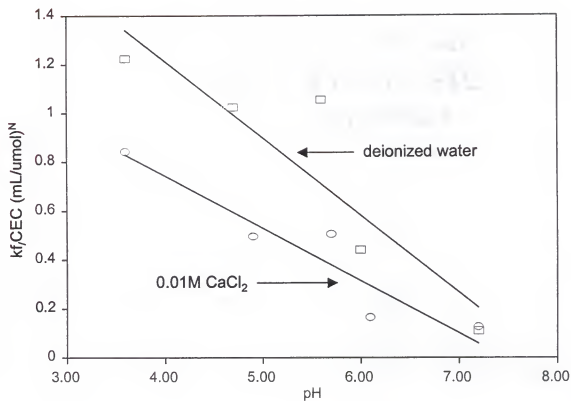


Figure 5.4. Effect of equilibration in 0.01M CaCl₂ and deionized water □ for quinoline on 5 soils.

partitioning, based on the exchange capacity and the organic carbon content according to equation 5.4.

$$S_T = \frac{S_{\max} K_L (BH^+)}{(1 + K_L (BH^+))} + K_{oc} f_{oc} (B^0). \quad (5.4)$$

All the variables in eq. 5.4 have been identified previously. For soils, S_{\max} was approximated by the CEC, and k_L was an optimized empirical parameter. The concentrations of the ionized and neutral species were determined from the pH and the pKa:

$$(BH^+) = \frac{B_T}{1 + 10^{(pH-pKa)}} \quad (B) = \frac{B_T}{1 + 10^{(pKa-pH)}}$$

There was no alternative to optimization of k_L for soils, since reducing the pH to determine a value of k_L for each soil would necessarily influence soil properties. K_{oc} was determined from the octanol-water partitioning coefficient, K_{ow} , using the equation of Baker et al. (1997). These authors comprehensively examined the existing data relating K_{ow} and K_{oc} and determined relationships for a broad range of compounds on soils and sediments, including many compounds with K_{ow} values similar to that for quinoline.

Operationally, the entire isotherm was fit to the data for each soil-chemical combination through optimization of k_L . The individual contributions of the neutral and protonated species subsequently were determined from the two terms in the combined isotherm. Sorption of the ionic species, therefore, was subject to the availability of quinolinium cations, their "affinity" for exchange sites (k_L), and the exchange capacity. The neutral-species contribution to sorption is a function of the organic carbon partitioning coefficient and the soil's organic carbon content--both of which can be assumed constant for a given sorbent-sorbate combination. Therefore, the magnitude of

the partitioning term in eq. 5.2 is dictated by pH, which governs the relative availability of the neutral species for a given sorbent-sorbate combination; it is unaffected by the optimization of k_L .

As stated, K_{oc} for quinoline was determined from the octanol-water partitioning coefficient, which was evaluated across a range in aqueous pH from 3 to 10 (Fig. 5.5). K_{ow} attained a maximum value of 131.1 at a pH more than two units greater than the pK_a where the compound should be almost exclusively in the neutral form. This yielded a K_{oc} value of 89.6 ml/g. **Sorption of Quinoline in 0.01M $CaCl_2$**

Predictions from the combined isotherm were generally good and sorption reflected the anticipated speciation of the compounds according to eq. 5.4. In Fig. 5.6 the combined isotherm simulations of sorption data for quinoline on the Felda (pH 3.6) and the Webster (pH 7.2) soils are shown. The isotherm was highly curvilinear for the Felda soil suggesting a dominance of the ionic term in eq. 5.4. Sorption of the neutral species was negligible. At pH 3.6, greater than 95% of the chemical was ionized and, therefore, it was responsive primarily to adsorption/exchange.

By contrast, linearity of the isotherm for the Webster soil initially suggested a greater involvement of the neutral species in sorption. The extent of that involvement, however, was revealed by disassembling the isotherm into its component parts as expressed by eq. 5.4. The data shown in Fig. 5.7 suggest that, although partitioning played a role in sorption, the isotherm still was dominated by the exchange term. This was true despite ample organic carbon (3.84%) and a pH of 7.2 where >99% of the chemical should be in the neutral form. The fractional contribution of the neutral species increased somewhat with increased aqueous quinoline concentrations, but this was due primarily to a small

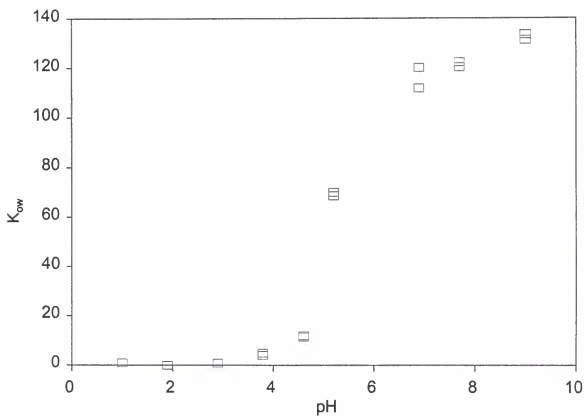


Figure 5.5 The octanol-water partitioning coefficient for quinoline as a function of pH.

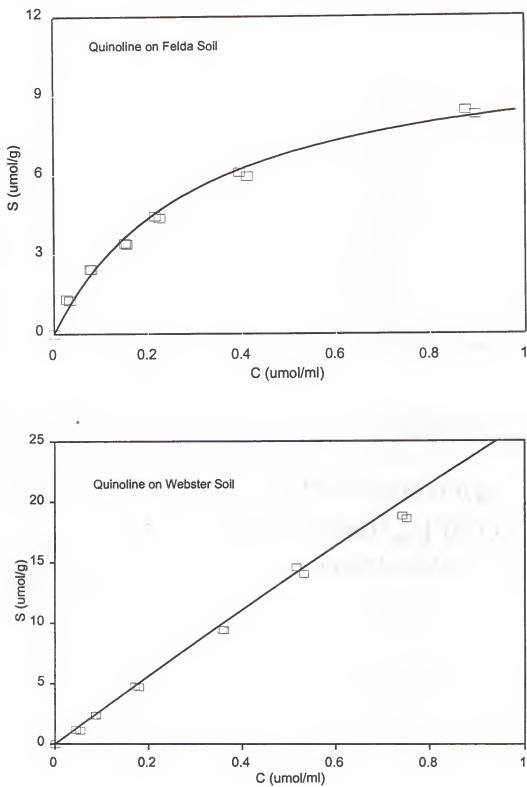


Figure 5.6. Combined isotherm simulations for quinoline on the Felda and Webster soils.

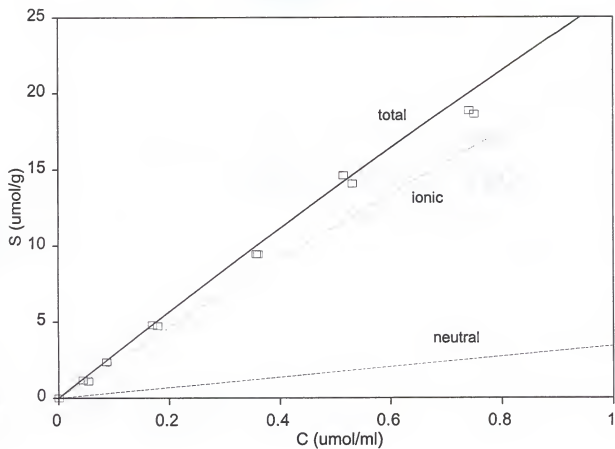


Figure 5.7. Dissembled isotherm for the Webster soil showing the contributions to sorption by the neutral and ionic quinoline species.

decline in the slope of the ionic component of the isotherm. At the highest measured aqueous solution concentration, sorption of the neutral species accounted for 12.7% of the total.

Therefore, based on pH alone, the contribution of the neutral species to sorption for the remainder of the soils studied would be expected to fall within this range established by the Felda and Webster soils, which represent the extremes in pH. The Mandarin soil, for example, had a pH of 4.9, indicating that about one half of the solution species should be in the neutral form. The data presented in Fig. 5.8 show that partitioning was evident, but both organic carbon content and pH were lower than for the Webster soil. Thus, the neutral species accounted for only a small fraction of total sorption-about 9.3% at the highest measured aqueous concentration. The Lochloosa soil also exhibited relatively weak base species sorption (Fig. 5.9). Sorption of the neutral species was only 12.9% of the total at the highest measured aqueous concentration.

The Eustis soil, however, exhibited comparable contributions to sorption from both the neutral and protonated species (Fig. 5.10). Customarily, this might be ascribed to an especially high pH or high organic carbon content, but these were only 6.2 and 0.64%, respectively. In fact, the pH was more than one full unit less than for the Webster soil, and the organic carbon content was more than five times less. The difference in results was due primarily to the magnitude of the organic carbon content *in relation* to the cation exchange capacity.

Cation Exchange Capacity and Organic Carbon Content

Use of the combined isotherm assumes that soil CEC and organic carbon content are determining variables affecting overall sorption. However, recall that exchange of the

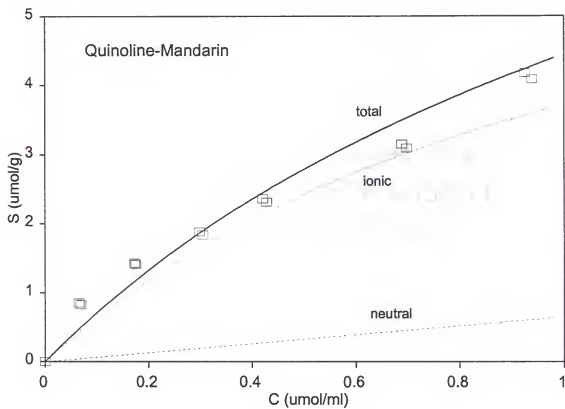


Figure 5.8. Sorption of quinoline on Mandarin soil (pH 4.9)

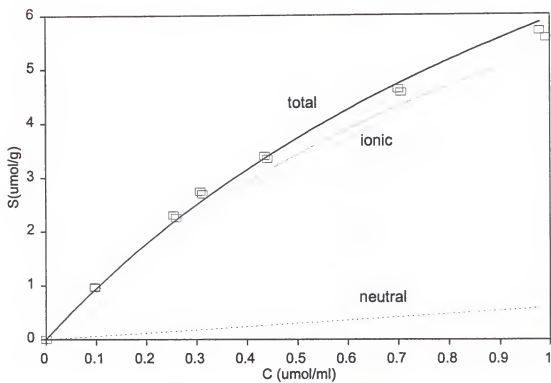


Figure 5.9. Contributions to quinoline sorption by the neutral and protonated species on the Lochloosa soil.

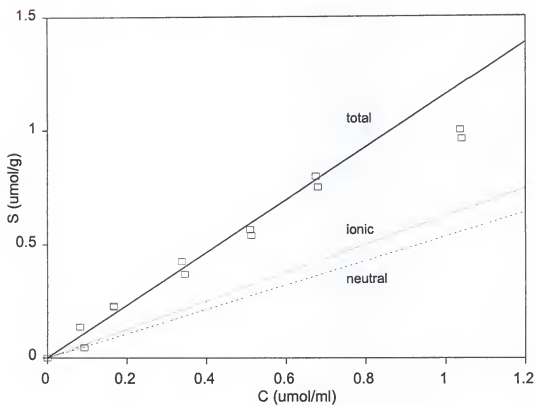


Figure 5.10. Contributions to quinoline sorption by the neutral and protonated species on the Eustis soil.

cation and partitioning of the neutral molecule are conjoined to some extent, and, if a compound has high exchange selectivity, it also will tend to be absorbed strongly on organic carbon. Thus, in addition to the relative strengths of adsorption and absorption, the relative proportions of the two associated sorbent components (rather than the absolute abundance of either one) ultimately will dictate the nature of sorption.

Table 5.3 lists the ratios of organic carbon to CEC for each soil as determined from the CEC in units of mmol/kg, and the organic carbon content (g/kg). For these soils, the Mandarin soil had the highest proportion of organic carbon (1.86 kg O.C./ mmol(-)), and the Webster soil the lowest (0.15 kg O.C./ mmol(-)). These are compared with the fractional contributions of the neutral species to sorption at the highest measured concentrations, and the with the corresponding fractions of the neutral species in the equilibrium solution.

Table 5.3. Organic carbon ratios of 5 soils in relation to sorption.

<u>Soil</u>	<u>pH</u>	<u>Organic Carbon/CEC Ratio</u> <u>(g O.C./ mmol (-))</u>	<u>Neutral Species</u> <u>In Solution (%)</u>	<u>Neutral Species</u> <u>Contribution (%)</u>
Felda	3.6	0.32	4.57	<1
Mandarin	4.9	1.77	48.8	9.8
Lochloosa	5.5	0.69	79.2	12.9
Eustis	6.1	1.05	93.8	43.6
Webster	7.2	0.15	99.5	11.9

The Eustis soil is unique among those examined in terms of both soil pH and the relative abundance of soil organic carbon. The pH is more than one full unit greater than the compound's pKa value, and the organic carbon/CEC ratio was high—second only to that for the Mandarin soil. As a result, neutral-species sorption for the Eustis soil

determined from the combined isotherm clearly eclipsed those for the other soils, and exceeded 40% of the total at high solution concentrations.

None of the other soils met this requirement with respect to *both* pH and sorbent composition. The Mandarin soil, for example, had the highest organic carbon content relative to CEC, but the soil pH was slightly below the pK_a of the compound. Conversely, the Webster soil had the highest pH, but also the lowest organic carbon content relative to its CEC. The pH of the Lochloosa soil exceeded the pK_a value somewhat, but this soil had a lower organic carbon/CEC ratio.

With respect to the data for the Eustis soil, and based upon the results for the Mandarin and Webster soils in particular, it appears that there is a straightforward tradeoff between pH and the relative reactivity of organic carbon. Both the Mandarin and Webster soils had similar contributions to total sorption from the neutral species, but for opposite reasons—one because of high pH, and the other due to a relatively high proportion of organic carbon. It is necessary, therefore, to assess the relative impacts of these two factors on sorption.

Sorption of the Neutral Molecule: Comparison with 2-Methylpyridine and Acridine

To recapitulate, fractional sorption of the neutral species with respect to the cation is based on three factors: availability of the neutral species in solution (pH), the relative abundance of organic carbon on the sorbate (organic carbon ratio), and the strength of absorption of the neutral molecule relative to adsorption of the cation. In the present context, the concern is with the relative strength of absorption. Manifestly, it is necessary to delineate the influences of pH and the organic carbon ratio more completely.

Two concurrent strategies were employed. The first was to moderate the influence of pH across soils through the employment of two morphologically similar N-heterocycles: 2-methylpyridine (1 ring) and acridine (3 rings). The pK_a values for 2-methylpyridine (6.00), quinoline (4.92), and acridine (5.68) correspond quite closely with the pH values of the Eustis, Mandarin, and Lochloosa soils, respectively. Therefore, the cation and neutral base species were essentially equally available in solution for these three soil/chemical combinations, limiting differences in neutral-species sorption arising from differences in their availability relative to the cation. The second strategy was to normalize sorption of the neutral species to the organic carbon/CEC ratio as opposed to the traditionally applied normalization to organic carbon *content*.

Earlier research (Zachara et al., 1986; Banwart et al., 1982) suggested that although the mechanisms of sorption were fundamentally similar for compounds like methylpyridine, quinoline and acridine, the relative strengths of adsorption and absorption for these compounds were essentially dissimilar. Recall again, however, that the paired influences of electrostatics and non-coulombic interactions on sorption of the cation link its fate to that of the neutral molecule, moderating disparities between the strengths of the two sorption mechanisms across compounds in a homologous series (Fig. 5.2).

Normalization to the organic carbon ratio

In Table 5.4 the percentages of overall sorption contributed by the neutral species for the three soil/chemical combinations are listed. The percentages were determined from the combined isotherm at the highest common equilibrium solution concentration, which was set by acridine. The solubility of acridine is limited, and its overall sorption

was high, which attenuated its concentrations in solution compared to quinoline and 2-methylpyridine. These values are compared with the percentage of neutral species sorption following normalization to the sorbent organic carbon/CEC ratio (% neutral species sorption/organic carbon ratio).

Table 5.4. Neutral species sorption normalized to the organic carbon ratio.

	<u>Neutral Species Sorption (%)</u>	<u>Normalized to th Organic Carbon/CEC Ratio (%)</u>
Methylpyridine-Eustis	5.79	5.49
Quinoline-Mandarin	9.79	5.26
Acridine-Lochloosa	3.71	5.38

Sorption of the neutral species was weak for all three soil/chemical combinations at this concentration (0.033 $\mu\text{mol/mL}$) as shown in Table 5.4 and Fig. 5.11. Also, the variability among the values, although not dramatic, was not related to the number of rings on the organic compound. However, normalization to the organic carbon/CEC ratio brought these values to an average of 5.37% of total sorption (Fig. 5.12), suggesting that the relative degree of neutral-species sorption for the three different combinations was dictated more by sorbent characteristics (i.e., the organic carbon/CEC ratio) than by characteristics of the chemicals.

The Effect of pH

Data from the previous section suggested that when the neutral and protonated species of the three N-heterocycles were equally available in solution, the cation was 17.6 times more strongly sorbed than the neutral molecule (based on 5.37% neutral sorption). Assuming that identical sorption mechanisms are afforded greater or lesser opportunity to operate depending upon soil pH, and also assuming the same relative strength of adsorp-

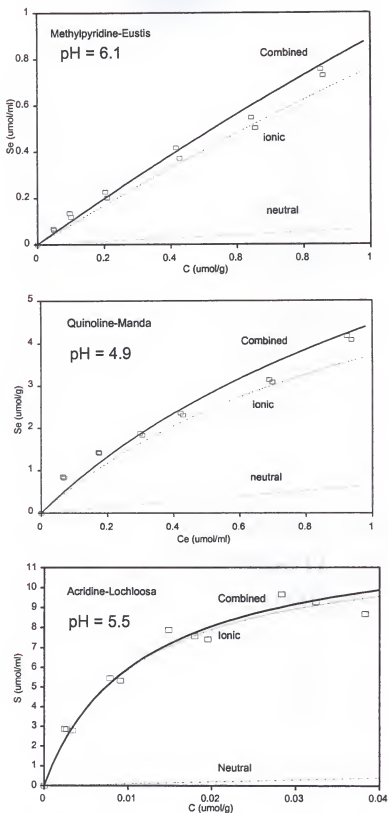


Figure 5.11. Comparison of three chemicals at pH values near the pKa value.

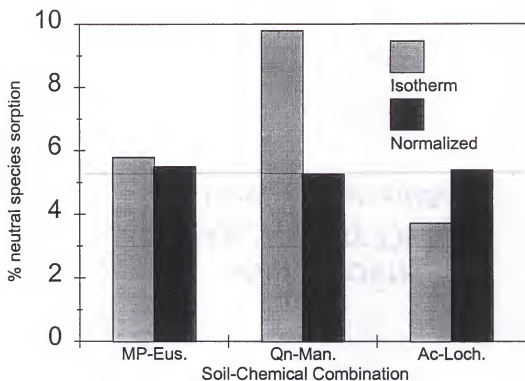


Figure 5.12. Neutral species sorption before and after normalization to the organic carbon ratio.

tion over absorption for the three compounds, the neutral species contribution to sorption at other availabilities of the cation and base forms can be calculated.

Total sorption can be assumed equal to the sum of the contributions from both the neutral and protonated species:

$$S_T = S_{\text{Neutral}} + S_{\text{Protonated}} \quad (5.5)$$

Sorption of the neutral and protonated species at a single concentration can be described by equations 5.6 and 5.7.

$$S_{\text{Neutral}} = k_d^\circ (B^\circ) \quad (5.6)$$

$$S_{\text{Protonated}} = k_d^* (BH^+) \quad (5.7)$$

Assuming that the cation is 17.6 times more strongly sorbed than the neutral molecule, the sorption coefficients k_d° and k_d^* can be compared:

$$k_d^* = 17.6 k_d^\circ \quad (5.8)$$

In addition, the relative availability of the two species can be expressed by equation 5.9:

$$(BH^+) = (B^\circ)/10^{(pH-Ka)} \quad (5.9)$$

Therefore, the fraction of total sorption due to the neutral species can be determined from equation 5.10:

$$\frac{S_{\text{Neutral}}}{S_{\text{Total}}} = \frac{k_d^\circ (B^\circ)}{k_d^\circ (B^\circ) + k_d^* (BH^+)} \quad (5.10)$$

Substituting equations 5.8 and 5.9 yields:

$$\frac{S_{\text{Neutral}}}{S_{\text{Total}}} = \frac{k_d^\circ (B^\circ)}{k_d^\circ (B^\circ) + (17.6 k_d^\circ (B^\circ)/10^{(pH-pKa)})} \quad (5.11)$$

Rearranging leads to:

$$\frac{S_{\text{neutral}}}{S_{\text{Total}}} = \frac{k_d^{\circ} (B^{\circ})}{(1 + 17.6/10^{(\text{pH}-\text{pK}_a)}) k_d^{\circ} (B^{\circ})} \quad (5.12)$$

Canceling common terms in the numerator and denominator yields an expression that is dependent only on the distribution of the compound in solution.

$$\frac{S_{\text{neutral}}}{S_{\text{Total}}} = \frac{1}{(1 + 17.6/10^{(\text{pH}-\text{pK}_a)})} \quad (5.13)$$

Table 5.5 lists contribution to sorption from the neutral species expressed as a percentage from both direct calculation according to equation 5.13, and also determined from the dissembled combined isotherm for 12 soil/chemical combinations; Fig. 5.13 is a graphical representation. The pH and organic carbon content/CEC ratio were constant for Each soil, so the distribution of the neutral species for each soil/chemical combination was dictated solely by the pK_a value of the compound and the constant, 17.6.

Table 5.5. Percentage of total sorption ascribed to the neutral species.

Combination	% neutral sorption from the isotherm (normalized to organic carbon ratio)	% neutral sorption, calculated
2-methylpyridine/Mandarin	0.64	0.45
Quinoline/Mandarin	5.26	6.39
Acridine/Mandarin	1.29	1.07
2-methylpyridine/Lochloosa	5.24	3.46
Quinoline/Lochloosa	8.72	17.76
Acridine/Lochloosa	4.08	5.15
2-methylpyridine/Eustis	5.49	5.38
Quinoline/Eustis	43.74	46.23
Acridine/Eustis	20.20	14.64
2-methylpyridine/Webster	54.60	47.38
Quinoline/Webster	79.63	91.54
Acridine/Webster	34.96	79.61

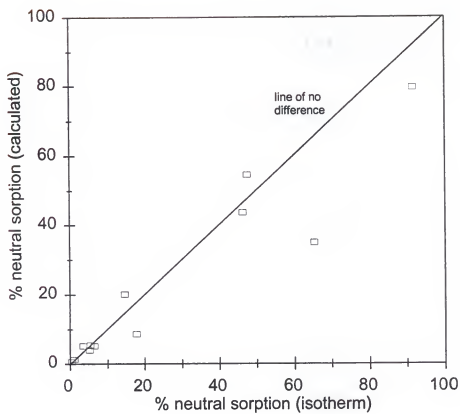


Figure 5.13 Comparison of neutral species sorption determined from the combined isotherm and calculated from a single value

The generally favorable agreement between values obtained from the combined isotherm and those calculated from the independent determination of absorption strength suggests the maintenance of equivalent relative absorption strengths for the cation and neutral species of the three homologous compounds. The most notable discrepancy was the acridine/Webster combination, but there were no consistent differences in the comparisons that would indicate a fundamental contradiction. Instead, the overall data appears to demonstrate that, when sorption was normalized to the relative abundance of organic carbon compared to the CEC and the availability of the neutral molecule in solution, fractional sorption of the neutral species of these compounds was comparable.

Optimization of K_L and the Role of Exchange in Adsorption

The employment of three N-heterocycles also provided additional corroboration for the assumption that adsorption is primarily a cation exchange process. Both the present examination and those by earlier investigators (Zachara et al., 1986; Zierath et al., 1980) suggested that adsorption of quinolinium and related compounds was largely a function of cation exchange based on correlation between the exchange-normalized Freundlich coefficient and concentrations of the ionized species in solution (Fig 5.3). Data from the combined isotherm tends to support this argument.

Recall that the contribution of the protonated species to overall sorption was determined by optimizing k_L in equation 5.1 for the total isotherm, and then separating the terms for each component to sorption. In other words, the *magnitude* of the neutral species contribution to sorption was established before the optimization, which simply sets a value for k_L in the exchange term of the isotherm. Therefore, the *fractional* neutral species contribution (the fraction of total sorption) is affected by the optimization only

insofar as the optimization impacts the adsorption term. It is based solely upon the value of K_{oc} , the organic carbon content, and the fraction of the neutral species in solution. In this context, the cationic or adsorptive component to sorption is, in essence, the optimized residual of total sorption. Therefore, based on the tacit assumption that cation exchange is the primary agent of adsorption, it is reasonable to examine how well the optimization of the adsorption term, through k_L , reflects an independent measure of adsorption via cation exchange.

Table 5.2 and Fig. 5.3, alluded to earlier, showed the relationship between ring number on the organic cation and the exchange coefficient, K_{ex} . They suggested a decline in exchange energy with ring number, which was mirrored by the octanol-water partitioning coefficient (Zachara et al. 1990). Similar plots for k_L obtained from the present data are shown in Fig 5.14. The magnitudes of k_L and K_{ex} determined by Zachara et al. (1986) are, of course, not identical, since the sorbent phases are different. However, the decline in k_L roughly parallels that of K_{ex} , suggesting that k_L bears a relation to the exchange coefficient. This further supports the earlier assumption that the adsorptive component to overall sorption is largely a cation exchange phenomenon and that CEC is one of the governing variables. The relation also helps to establish the legitimacy of the Langmuir isotherm as a means of quantifying this component of the overall sorption process.

Conclusions

Exchange dominance of organic base sorption even at pH levels well in excess of the sorbate pK_a value has persuaded several investigators (e.g. Nichols and Evans, 1991) to infer that surface-facilitated ionization essentially increases the concentration of the

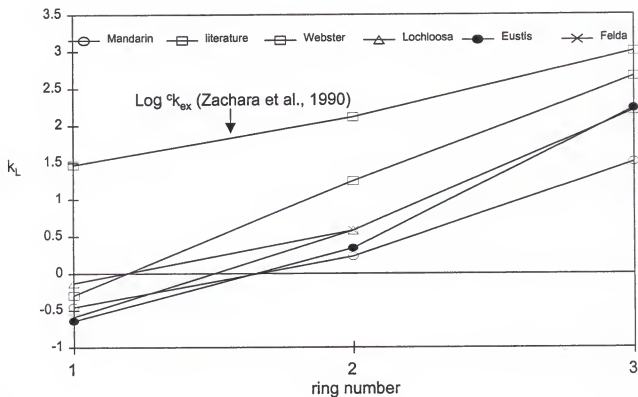


Figure 5.14. Relationship between the sorption coefficient k_L and the conditional exchange coefficient $c_{k_{ex}}$ for three chemicals with increasing ring number and five soils.

protonated species in the adjacent solution over that in bulk solution. The evidence in support of this is compelling (Chapter 1). However, as early as 1970, Mortland (1970) suggested that dominant soil or clay mineral uptake of protonated organic bases over the neutral molecule is likely more rudimentary and arises from simple considerations of their relative sorption strengths.

The present examination supports this view. Appreciation of the relative sorption of the neutral molecule plainly requires prudent consideration of the elements necessary for it to manifest. For 2-methylpyridine, quinoline, and acridine these elements involve the appropriate relations between the primary sorbent components and availability of the neutral molecule in solution.

In effect, adsorption of the cation generally will be favored over absorption of the neutral base, due to the combination of Coulombic and non-Coulombic components. Therefore, we require some method to "level the playing field", either through judicious choice of the soil/chemical combination or through indirect expression of the relevant relationships (for example, normalization to the organic carbon/CEC ratio).

APPENDIX A ISOTOPIC EXCHANGE

The derivation below indicates how the cation exchange capacity of organoclays was determined using isotopic exchange. The parameters for isotopic exchange are as follows:

^{40}Ca = calcium

^{45}Ca = radiolabeled calcium

V = volume of solution added to soil (mL)

m = mass of soil (g)

C_o = concentration of ^{40}Ca (umol /mL)

C_o^* = concentration of ^{45}Ca (counts per min./mL)

S = amount ^{40}Ca sorbed (umol/g)

S^* = amount ^{45}Ca sorbed (cpm/g)

$f = C_o/C_o^*$ (umol/cpm)

It is assumed that ^{45}Ca behaves exactly as ^{40}Ca , both in solution and on the soil.

Therefore, at equilibrium,

$$\frac{S}{C} = \frac{S^*}{C^*} \quad (\text{A.1})$$

$$\frac{C}{C_o} = \frac{C^*}{C_o^*} \quad (\text{A.2})$$

and,
$$S = \frac{V}{m} [(C_o^* - C^*)f] + C \frac{S^*}{C^*} \quad (\text{A.3})$$

Employing eqs. A.1 and A.2, allows eq. A.3 to be written in terms of C^* and C_o^* , such that,

$$S = \frac{V}{M} [(C_o^* - C^*)f + C_o(1 - (C^*/C_o^*))] \quad (\text{A.4})$$

Several initial calcium chloride solutions were then spiked with small amounts of radiolabeled calcium. Following soil equilibration, the concentration (cpm) of the remaining solution radiolabeled calcium was determined by liquid scintillation counting. Since the two isotopes behave the same in solution and on the soil, the original relative proportions of the isotopes determined by the spike are maintained. Therefore, both sorbed and solution concentrations can be determined. The cation exchange capacity was indicated by the sorption maximum determined from regression of the linearized Langmuir isotherm.

APPENDIX B DERIVATION OF THE COMBINED ISOTHERM AND THE SORPTION COEFFICIENT

Dissociation of the organic base in solution can be represented:



where, BH^+ is the protonated base; B^0 is the neutral base; and H^+ is the hydrogen ion. The equilibrium relationship is:

$$K_a = \frac{(\text{B}^0)(\text{H}^+)}{(\text{BH}^+)} \quad (\text{B.2})$$

where, K_a is the acid dissociation constant. Taking the logarithm of both sides yields:

$$\text{Log } K_a - \text{Log } (\text{H}^+) = \text{Log } ((\text{B}^0/\text{BH}^+)) \quad (\text{B.3})$$

The equation can be rearranged as follows:

$$\text{pH} - \text{p}K_a = \text{Log } ((\text{B}^0/\text{BH}^+)) \quad (\text{B.4})$$

Therefore,

$$10^{(\text{pH}-\text{p}K_a)} = (\text{B}^0/\text{BH}^+). \quad (\text{B.5})$$

The fraction of the cationic species (F_I) in solution can be represented:

$$F_I = \frac{(\text{BH}^+)}{(\text{BH}^+) + (\text{B}^0)} \quad (\text{B.6})$$

Substituting for B^0 in eq. B.6 using eq. B.1 and rearranging yields:

$$F_I = 1 / 1 + 10^{(\text{pH}-\text{p}K_a)} \quad (\text{B.7})$$

The fraction of the neutral species (F_N) in solution can be derived similarly, such that,

$$F_N = \frac{10^{(\text{pH}-\text{p}K_a)}}{1 + 10^{(\text{pH}-\text{p}K_a)}} \quad (\text{B.8})$$

If ϵ is set equal to $1+10^{(\text{pH}-\text{pK}_a)}$, and the total sorbate concentration $C_T = (\text{BH}^+) + (\text{B}^0)$, then the concentration of the ionic and neutral species can be represented:

$$C_I = \frac{C_T}{\epsilon} \quad \text{and} \quad C_N = C_T \frac{(\epsilon-1)}{\epsilon} \quad (\text{B.9})$$

Based on eq. B.9, the combined isotherm can be represented as a function of the total concentration:

$$S_T = \frac{S_{\max} k_L (C_T/\epsilon)}{1 + k_L (C_T/\epsilon)} + K_{\text{oc}} f_{\text{oc}} C_T (\epsilon-1)/\epsilon \quad (\text{B.10})$$

where, S_T is total sorption, S_{\max} is the sorption maximum, K_{oc} is the organic carbon partitioning coefficient, f_{oc} is the fraction of sorbent organic carbon, and k_L is an empirical coefficient.

The sorption coefficient (k_d) is equal to the derivative of total sorption with respect to total concentration in equilibrium solution (dS_T/dC_T). This yields:

$$k_d = \frac{S_{\max} k_L \epsilon}{(\epsilon + k_L C_T)^2} + K_{\text{oc}} f_{\text{oc}} \frac{(\epsilon-1)}{\epsilon} \quad (\text{B.11})$$

such that k_d is a function of pH, the total concentration in solution (C_T), and the compound pK_a value. Therefore, the magnitude of the sorption coefficient with respect to the solution pH will depend on both terms, while it is only dependent upon the ionic term with respect to the concentration.

APPENDIX C SORPTION PARAMETERS

The following table lists the parameters used in the preceding equations describing sorption of quinoline on both soils and organoclays.

Table C.1. Parameter descriptions.

Parameter	Description	Units
S	Sorbed chemical concentration	umol/g
C	Solution chemical concentration	umol/mL
S _{max}	Sorption maximum	umol/g
k _L	Empirical Langmuir coefficient	n/a
K _{oc}	Organic carbon partitioning coefficient	mL/g
f _{oc}	Fraction of sorbent organic carbon	g OC/g soil
QH ⁺	Solution concentration of ionized quinoline	umol/mL
Q	Solution concentration of neutral quinoline	umol/mL
K _f	Freundlich sorption coefficient	mL/g
N	Freundlich exponential coefficient	n/a
k _d	Overall sorption coefficient (S/C)	mL/g
K _a	Acid dissociation constant	n/a
pK _a	Negative Log of the acid dissociation constant	n/a

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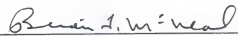
BIOGRAPHICAL SKETCH

Born in Illinois, James Bonczek has lived in Florida for more than 30 years. He received a Bachelor of Arts in Education and a Master of Science Degree in Soil and Water Science from the University of Florida. His current professional interest is primarily teaching.


I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


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Brian McNeal
Professor of Soil and Water Science

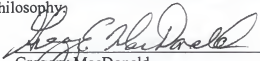
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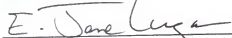

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This dissertation was submitted to the Graduate Faculty of the College of Agricultural and Life Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May, 2002



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